N.M.R. OF HETEROATOMIC STRUCTURES OF COAL AND COAL PRODUCTS

by

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Submitted for the degree of Doctor of Philosophy

University of Warwick

Departement of Chemistry

September 1988

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ACKNOWLEDGEMENTS

I would like to thank Dr. Oliver Howarth and Dr. Paul Burchill for their constant encouragement and advice which they have provided throughout the course of this work.

Thanks are also due to all the staff at the coal research establishment, especially John Hodges for his helpful comments on the ^{23}Na work, and the members of their analytical group who provided the ultimate and proximate analyses on the coal and coal products.

The financial assistance of the S.E.R.C. and British Coal is gratefully acknowledged.

DECLARATION

The work described in this thesis is the original work of the author except where acknowledgment is made to work and ideas previously described. It was carried out in the Department of Chemistry, University of Warwick and the coal research establishment of British Coal between October 1985 and September 1988 and has not been submitted previously for a degree at any institution.

SUMMARY

This thesis describes various applications of high field n.m.r. for the elucidation of coal structure, and concentrates on discovering the chemical environments of the heteroatoms in coal i.e. those elements other than carbon and hydrogen.

Chapter 2 describes how hydroxyl groups may be converted to trimethyl siloxyl groups, observation of which by ^{29}Si n.m.r. allows one to determine the types of hydroxyl functionalities present in the original material. Such derivatization methods are well known. However trimethyl siloxyl groups give ^{29}Si resonances that have predictable chemical shifts and so the derivative spectra of complex coal tars and extracts are easy to interpret. Using this technique we have investigated the nature of hydroxyl groups in a rank series of coal tars. This has given us some insight into the way the hydroxyls are affected by coalification.

Chapter 3 is a demonstration of the use of ^{1}H n.m.r. as a detector for H.P.L.C.. This has two principle novelties over previous work. Firstly it does not involve building a special probe and secondly, the data is presented as a contour plot of intensity vs. retention time and chemical shift. This method has been used to investigate the nature of several tar fractions and complements the derivatization technique of chapter 2.

The final chapter shows how the nature of sodium in coal was determined by ^{23}Na MAS-NMR. By using the information contained in the chemical shift and linewidths of raw and dried coal it was concluded that sodium exists bound to the surface of coal pores by oxygen functions such as carboxylates and phenoxides. It does not exist as sodium chloride microcrystals as once thought.

PUBLICATIONS

Parts of the research described in this thesis have appeared in the scientific literature as follows:-

1) "Solid state n.m.r. of Na and Al in coal".
Oliver W. Howarth, Giles S. Ratcliffe and Paul Burchill.
FUEL 66. 33 - 39. (1987)

2) "sodium and aluminium MAS-NMR in coal and coal ash".
Oliver W. Howarth, Giles S. Ratcliffe.
1987 International Conference on coal science.
ELSEVIER 1987 p143 - 147.

The material presented in chapters 2 and 3 of this thesis is at present being prepared for publication in the journal FUEL.

Abbreviations

a.d.	as determined
Ar	Aromatic ring
C.O.S.Y.	2-D shift correlation experiment
C.R.E.	Coal Research Establishment
δ	chemical shift
(d)	doublet
d.a.f.	dry ash free
d.b.	dry basis
DEPT	Distortionless enhancement by polarization transfer
d.m.m.f.	dry mineral matter free
D.M.S.O.	dimethyl sulphoxide
F.I.D.	Free Induction Decay
gc-ms	gas chromatography-mass spectrometry
H.M.D.S.	hexamethyl disilazane
H.P.L.C.	High performance liquid chromatography
I	nuclear spin quantum number
I.N.E.P.T.	Internuclear enhancement by polarization transfer
J	Scalar coupling constant
L	orbital angular momentum quantum number
L.C.-M.S.	Liquid chromatography-mass spectrometry
L.C.-N.M.R.	Liquid chromatography-nuclear magnetic resonance spectroscopy
(m)	multiplet
M.A.S.	magic angle spinning
Me	methyl
n.O.e.	nuclear Overhauser effect
n.m.r.	nuclear magnetic resonance
P.A.H.	Polyaromatic hydrocarbons
p.p.m.	parts per million

(s)	singlet
T_1	longitudinal relaxation time constant
T_2	transverse " " "
(t)	triplet
T.H.F.	tetrahydrofuran
T.M.S.	trimethyl-silyl or Tetramethylsilane
w.r.t.	with respect to

1.1 WHY STUDY COAL?

Coal is undoubtedly the most important natural resource to be found in the British Isles, there being sufficient to provide for our electrical power for 300 years. It is however a poorly understood material from a chemical viewpoint despite its widespread use.

There are a wide variety of different coals found worldwide ranging from the soft brown coals of Australia to hard Anthracites. These two materials appear to be completely unrelated, however they are both made up of fossilized plant remains. This forms the basis of a definition of coal as

> "a combustible solid. usually stratified, which originated from the accumulation, burial, and compaction of partially decomposed vegetation in previous geologic ages". [1]

The aim of coal science is to provide an accurate and complete description of the chemical nature of coal. This is an interesting discipline in its own right but also provides the basic information which is required for beneficial coal utilization.

Our particular interest in the subject was to try and use modern N.M.R. spectroscopy to solve problems concerning the heteroatoms in coals. These may be defined as those atoms present excluding carbon and hydrogen and including the mineral matter. The nature of the mineral matter is important as it is the cause of much boiler fouling and corrosion. The organic functional groups present in coal e.g. amines, hydroxyls, etc. affect the performance of coal liquifaction processes, the perfection of which is an area of some technological importance.[2]

The following sections give a description of the variety, classification, structure and genesis of coals as it is understood at present. The use of N.M.R. methods to elucidate coal structure is then discussed as a prelude to a description of our work done in collaboration with the coal research establishment (C.R.E.) of British coal.

1.2 CLASSIFICATION OF COALS. COAL RANK

The large range of different types of coal reflects the many changes that occur during the metamorphosis of plant material to anthracites. Coals are classified according to the degree of metamorphosis that has occurred, known as coal rank. A brown coal which has changed relatively little from peat is of low rank whereas anthracites are of high rank.

There are several parameters that may be used to define coal rank. The one used throughout this work is the carbon content of the coal determined on a dry, mineral matter free basis. Coals are found with %C between 65% and 95%. As coalification proceeds the material passes through several identifiable stages:

%C = 65% - 75% lignite or brown coals which are very high in both oxygen and moisture. These are light and brittle materials which have undergone only the first stages of coalification.

%C = 75% - 93% Bituminous coals. The coals found in Britain are mostly of this type. These are the familiar shiny coals used, as are most coals, for power generation.

%C 93% Anthracites: the last stage of coalification produces these graphite-like materials.

A description of how other analytical parameters depend on carbon content is needed to complete explanation of what is meant by coal rank. This is given in figure 1 in graph form; the data is from the analysis of the 15 coals used in our study of sodium in coal (chapter 4).

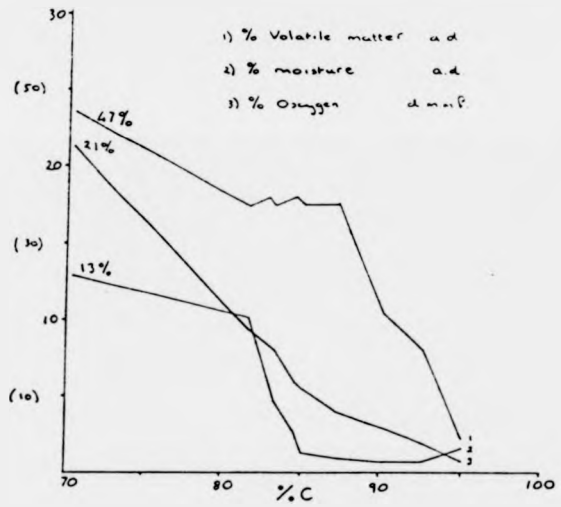


Figure 1

1.3 COALIFICATION: FROM PEAT TO ANTHRACITE

In order to describe the formation of coal one must first understand the nature of its precursor, peat. This is a material consisting of partly decayed organic matter that lived in wetland areas. In order for peat to be laid down the organic material must be dying faster than it is being removed by erosion and/or consumption by micro-organisms. This means that peat is only formed from plants and animals living in stagnant waters, since in flowing waters autooxidation and erosion of decayed material will prevent sedimentation occurring. As the plants die they pass through several stages of decomposition. Initially they float in the upper 2 metres of water which is inhabited by aerobic bacteria. These live off the dead plant material, thereby releasing CO_2. This process affects cellulose in particular and so the humic

acids, or humus, produced have greater concentrations of waxes, resins, spores and carbon rich barks than the original plant material.[3]

As more growth occurs on the surface of the wetlands the humus is buried deeper and aerobic decomposition ceases due to lack of oxygen. The humus is then altered by anaerobic fermentation, or putrifaction. The microorganisms responsible for this live by taking the carbon they require from the decaying material and in the process release H_2S, NH_3 and CO_2. The formation of pyrite, which is often found in coal, is associated with putrifaction. The humus has become alkaline and reducing in nature, this causes reduction of Fe^{3+} to Fe^{2+} which in the presence of H_2S causes many forms of iron sulphide to be produced.[4] The process of putrifaction begins at a depth of about 2 metres and is complete at about 10 metres after which no further biological processes occur[5]. The product of these processes is peat, which when buried and heated turns to coal. About 6 feet of peat are required to produce 1 foot of coal, such is the compaction that occurs on coalification.[6]

At this point it is appropriate to show the changes in elemental composition as one proceeds from peat to anthracite:

Rank	%C	%H	%O	%N	%S
Peat	55	6	30	1	1.3
Lignite	72.7	4.2	21.3	1.2	0.6
Medium volatile bituminous	88.4	5.0	4.1	1.7	0.8
Anthracite	93.7	2.4	2.4	0.9	0.6

Source ref 7

The coalification process begins when geological change causes a peat deposit to be buried and thus have its temperature and pressure raised. The metamorphosis is essentially a continuous process, where one type of coal blends into another.[8] The principal chemical processes that occur are decarboxylation, which occurs mainly in the early stages of coalification, dehydration and demethanation. The demethanation is the process where aromatic rings condense to form larger aromatic hydrocarbons, this releases methane. This is the source of methane that collects while mining coal and has caused several underground explosions. It is demethanation that causes coal to become more like graphite as coalification proceeds.

As yet we have not mentioned to what extent peat must be heated and compressed in order that coal will form. Fox[9] has investigated this and concluded that at 30°C a lignite containing 75% carbon could be formed in 8.5 million years, and an anthracite in 0.5 million years at 150°C. These conclusions indicate that extreme conditions are not necessary for coal formation as was once thought. Maximum temperatures that coals have been subjected to may be estimated from the types of structures found e.g. fossil cuticles decompose above 250°C. Using such methods Francis [10] deduced that medium rank bituminous coals had been subjected to not more than 280°C. The important point is that coal rank is dependent on both the maximum temperature experienced by a coal and the time it is kept at such a temperature. The effect of pressure on coal rank is less certain in that high pressure will slow down processes such as methanation, however the temperature associated with such depths will speed it up. The final piece of background information on coal needed before moving on to discuss N.M.R. methods and coal is that of its basic molecular structure.

1.4 MODELS OF COAL STRUCTURE

The chemical nature of coal is best illustrated by its behaviour when treated with organic solvents. It is largely insoluble in any solvent. For example chloroform will extract ~10% of the total mass, and pyridine ~30%.[11] This insolubility is strong evidence tht coals are cross-linked polymers. The extractable material is non-polymeric and is trapped by the macromolecular structure. These two parts of coal are often referred to as the stationary and mobile phases of coal. When coal is treated with pyridine it is observed to swell.[12] This is due to the pyridine penetrating the coal and pushing apart many hydrogen bonds. Such behaviour is typical of many cross-linked polymers and explains why pyridine extracts a greater proportion of the coal than chloroform.

We may therefore visualize coal as a sponge-like insoluble material that has soluble fragments contained within it. A commonly made assumption is that the mobile phase is representative of the stationary phase and therefore of the whole coal. The evidence for this is mostly circumstantial, for example it is known that the I.R. spectrum of pyridine extracts is similar to that of a whole coal.[13] The assumption is probably valid as long as one realizes that the stationary phase probably contains larger polyaromatic units than could be extracted even if they were not bound to the polymer.

Studies on the structure of solvent extracts have a long history and many structural features are well known. These have been collated by several works into models of a "coal molecule". These models express the atomic composition, aromaticity, and functionalities believed to

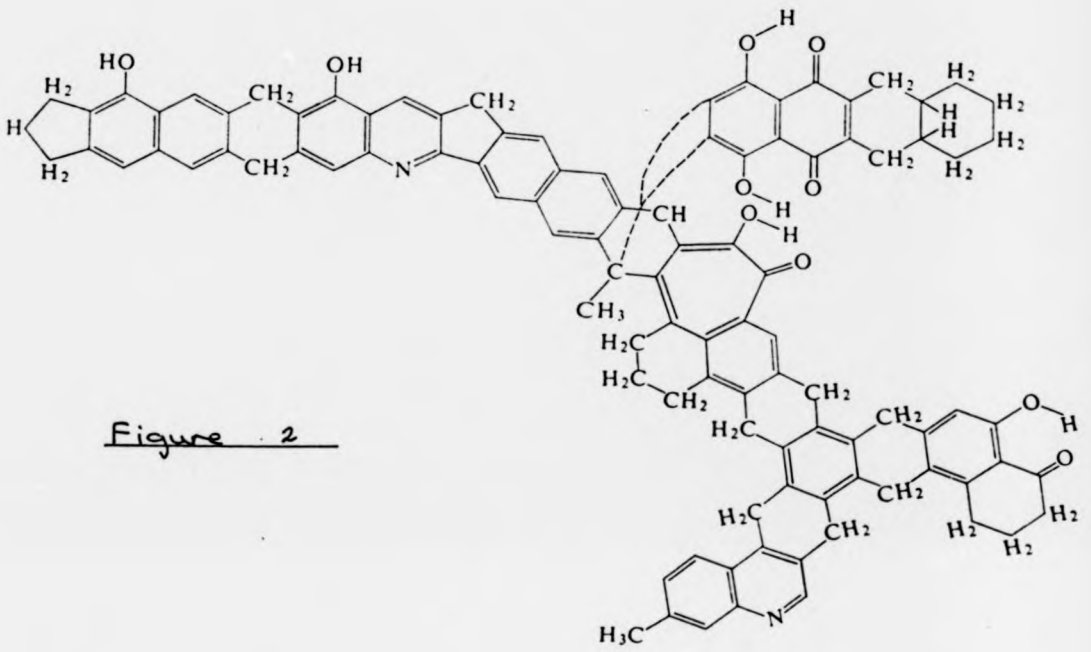
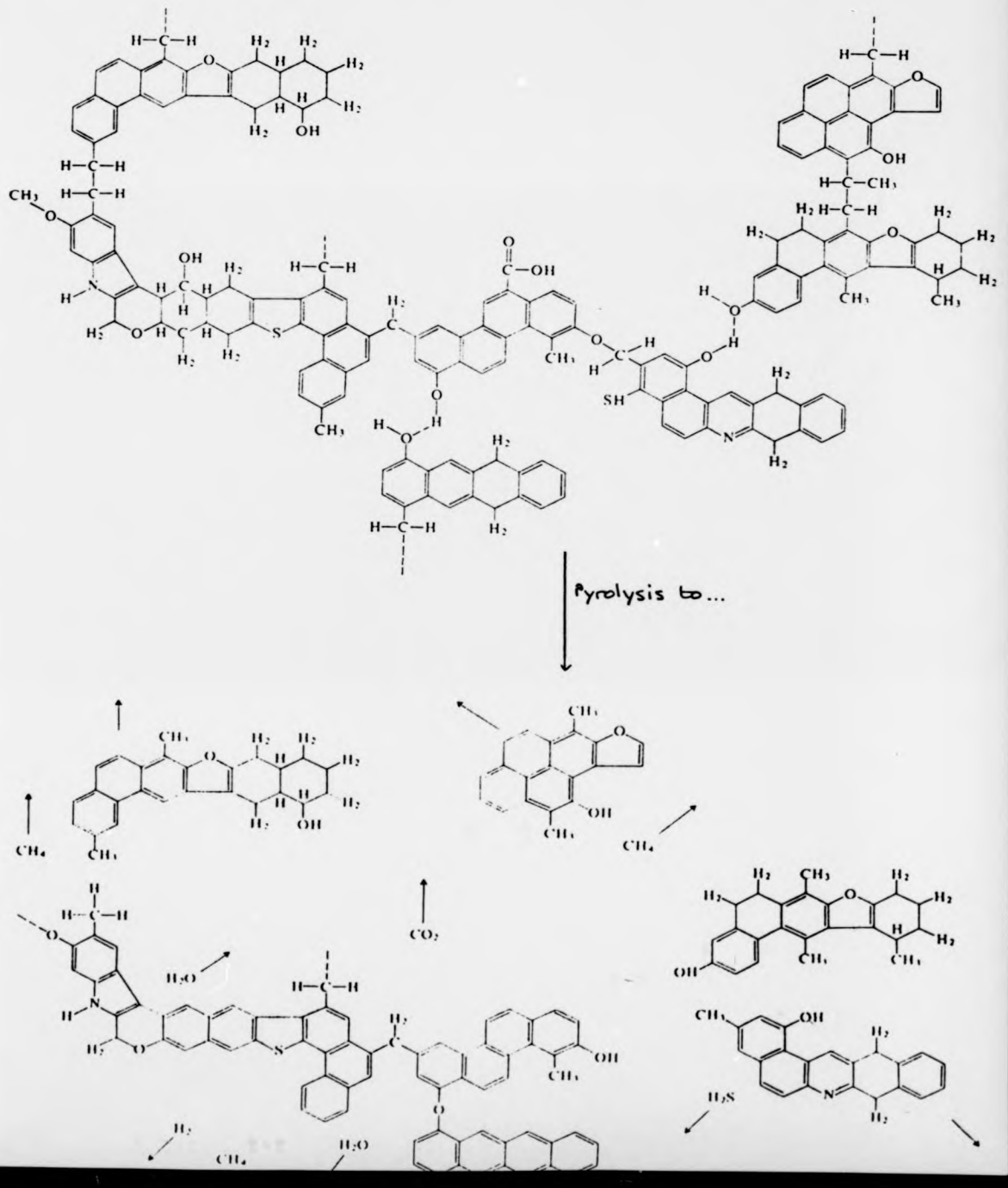


Figure 2

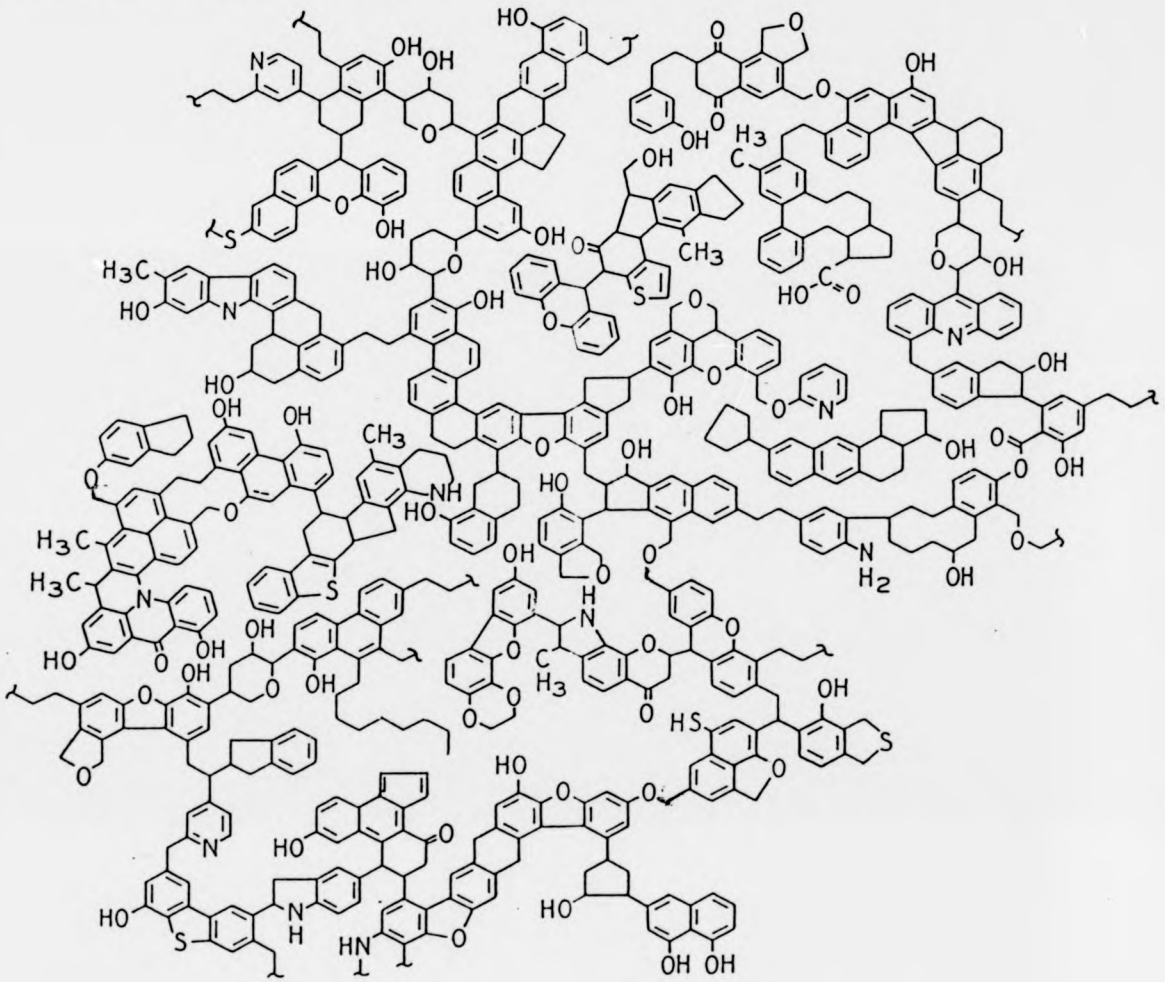
Figure 3



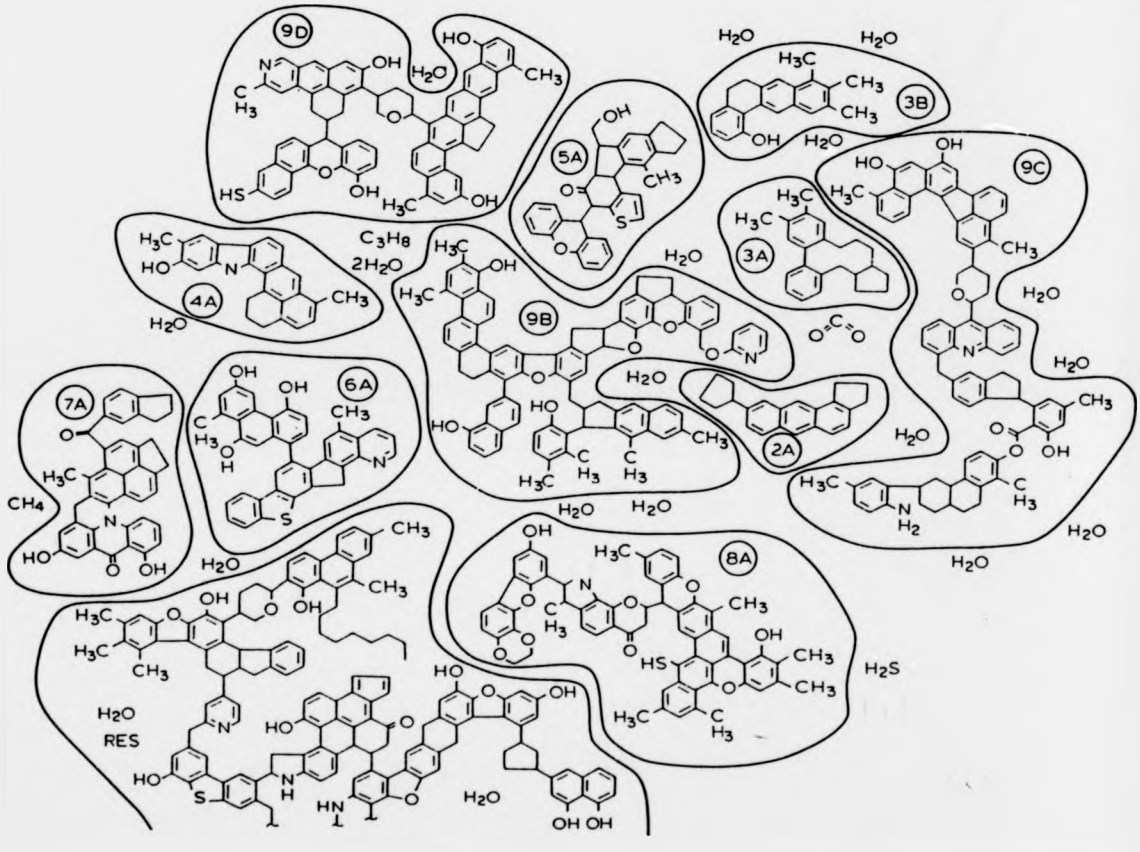
be present in coal. Their purpose is to illustrate the types of groups present in coal and to show some features of a coal's properties. Such a model is shown in figure 2 and is due to P.H. Given[14]. This is designed to show the 3-dimensional aspect of coal molecules. The model shows many of the functionalities expected, e.g. hydroxyls, and pyridines. Other coal models show how a coal fragment might behave under pyrolysis such as that of Solomon[15] (figure 3), and J.H. Shinn[71].

The model of J.H. Shinn (see overleaf) attempts to describe the behavior of a representative fragment of a coal (Illinois 6) under various liquefaction conditions. In order to mimic the experimental data adequately the fragment needs a molecular mass of 10,000 Daltons. From the elemental analysis of the coal the molecular formula is calculated to be $C_{661}H_{561}O_{74}N_{11}S_6$. The model structure is made up from several substructures which each embody the average composition data for one chromatographic fraction from the liquefaction process. These substructures are bound covalently to one another by bonds known to be labile under liquefaction conditions. The model also contains molecules not covalently bound to the fragment. These molecules may be extracted from the coal with solvents under mild conditions and make up the 'mobile' phase of the coal.

Reactive model of coal structure: J. H. Shinn[71]



The types and proportions of aliphatic and aromatic carbon atoms present in the model corresponds with that found in the native coal as determined by ^{13}C solid state N.M.R. The functional groups were then distributed according to their appearance in the liquefaction fractions. The effect of liquefaction on this model is shown below



When this model fragment is heated in a proton rich environment several reactions are thought to occur;

1) The oxygen held in alcohols is lost as water,
2) Phenyl-ethers are cleaved producing phenols,
3) Methylene bridges between aromatics are broken,
4) The proportion of aromatics increases.

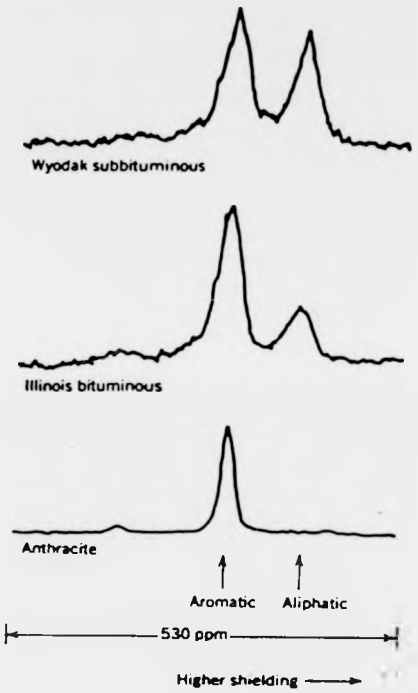
This model of coal structure is particularly interesting in view of our work on coal tars, and will be discussed again in Chapter 2, where some modifications are suggested.

These models give some idea of the complexity of coal and why coal products contain thousands of components. This is a major problem from an analytical viewpoint and makes identification of individual structures very difficult. As will be seen, N.M.R. spectroscopy can provide much information on both the gross aromaticity and carbon structure, and on the functionalities present, and as such is one of the most important tools in the endeavour to understand coal.

1.5 THE INVESTIGATION OF COAL STRUCTURE BY N.M.R.

The analysis of non-crystalline solids took a leap forwards with the development of techniques to observe ^{13}C using N.M.R. in solids. This is achieved by using a cross-polarization technique coupled with magic angle spinning (M.A.S.).[16] A rank series of coals have been observed using this technique by Maciel[17], the results of which are shown below.

^{13}C M.A.S NMR SPECTRA OF COALS (ref 17)

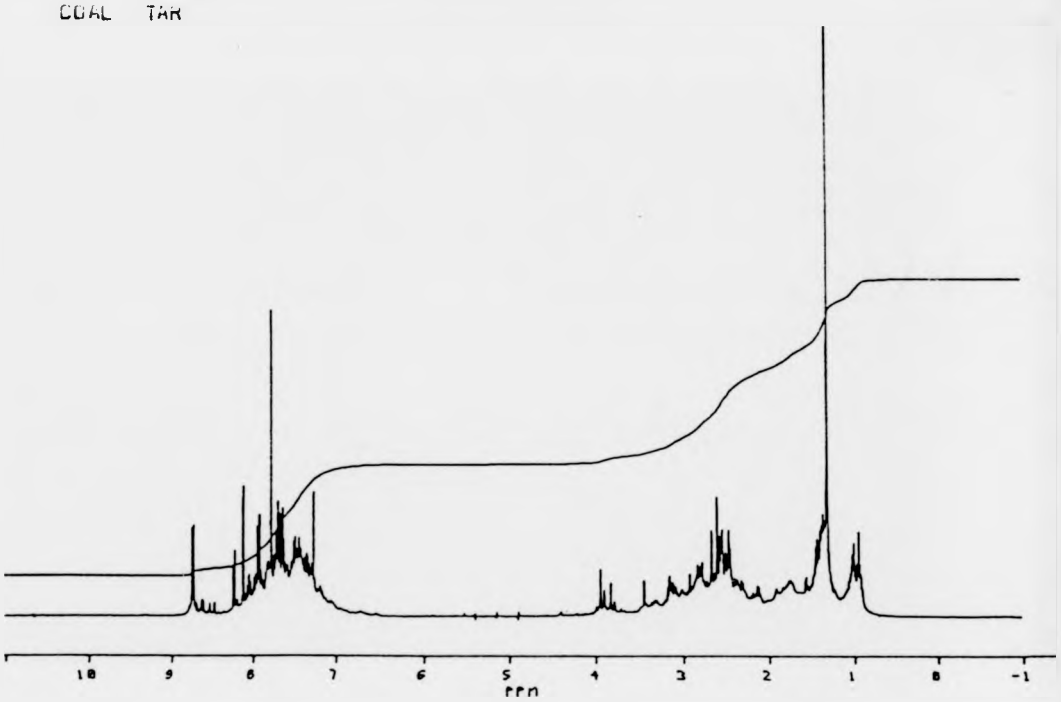


The wide variety of different structures present mean that only broad bands are observed. This in itself is a useful observation in that it proves that coal is not made up of a small number of specific subunits. The two bands observed correspond to aromatic and aliphatic carbon atoms and it is clear that sub-bituminous coals are only 50% aromatic while anthracites are very close to graphite. This is direct evidence that as coalification proceeds aliphatic moities are being converted to polyaromatic hydrocarbons. Indeed the % aromaticity of coals as determined by CP-MAS 13C NMR could be used as a measure of coal rank.

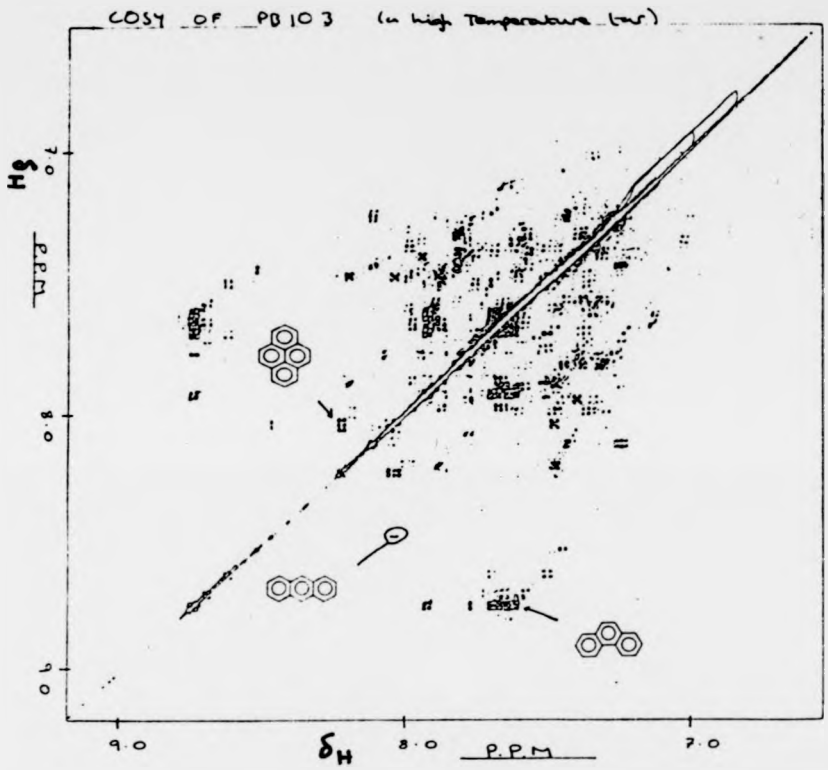
MAS-NMR techniques are particularly useful for the analysis of mineral matter and have revealed the chemical environment of sodium in coal, chapter 4.[18] It has also been used to investigate the types of alumino-silicates found in coal.[19]

The most common use of ^{1}H spectra on coal products is for determining the relative proportions of certain groups, e.g. aromatic protons, methyl aromatics, methyl aliphatics etc. This is because the normal proton spectrum is highly complex and only the gross features can be easily interpreted.

^{1}H N.M.R SPECTRUM OF THE AROMATIC FRACTION OF A COAL TAR



We have had some success however in using the 2-D technique of Correlation Spectroscopy or COSY. The variant used was that of Ernst[20] and produces a cross peak between 2 scalar coupled nuclei. This method was used to confirm the structures of various polyaromatic hydrocarbons (P.A.H.) detected by LC-NMR (chapter 3). An example of a COSY Spectrum is shown below. This is a 2-D plot of the aromatic region of the spectrum above and clearly shows the presence of several P.A.H.

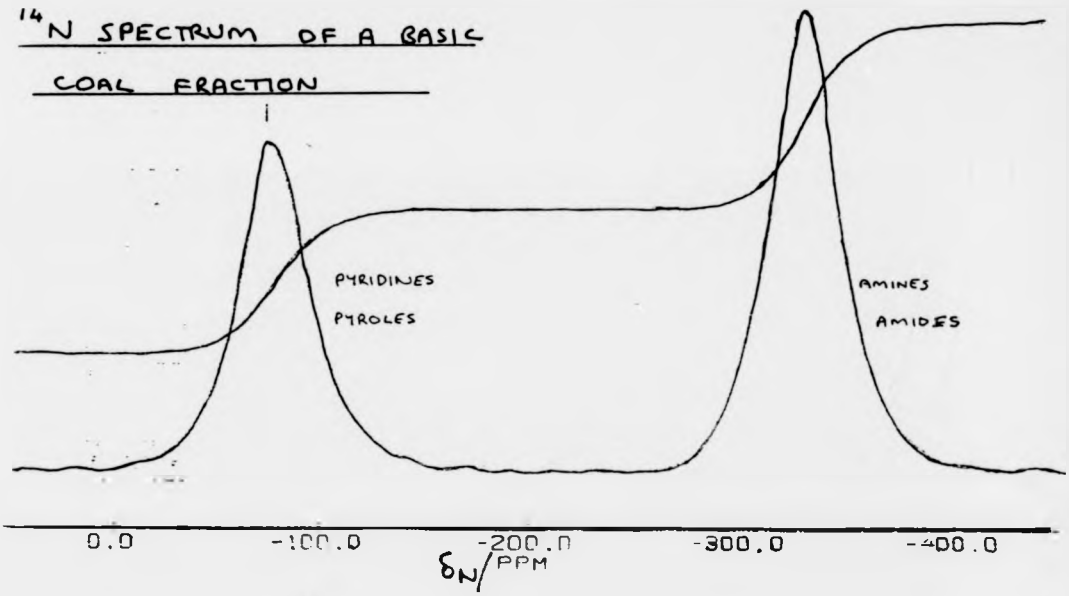


The detection of heteroatoms is difficult by direct NMR methods and so more indirect methods such as derivatization have been developed. These are explained in the following section.

1.6 DERIVATIZATION METHODS

As we have seen it is very difficult to determine the functional groups present in coal or coal products from ^{1}H or ^{13}C n.m.r. spectra alone. This is because the spectra are very complex and it is impossible to say which nearby groups have caused which chemical shifts of methylene, aromatic proton, etc. The atoms of the functional groups themselves are not good nuclei for observing by nmr. Oxygen is not possible at natural abundance for coal samples and neither is nitrogen-15. Nitrogen-14 can be detected but the linewidths are large due to it being a quaduropolar nuclei.[20] These spectra can determine the

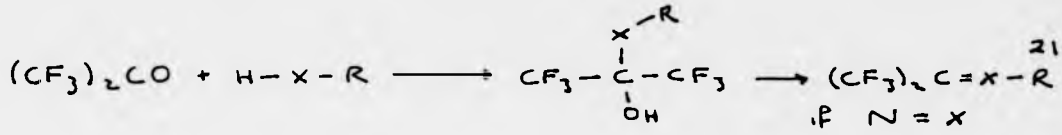
relative abundance of ring Vs amine nitrogen in a sample, as shown below.



It is clear therefore that in order to get a good profile of the functional groups present in coal products one must find a different approach.

The idea of derivatizations is to change the functional groups in a controlled manner into ones which contain n.m.r. active nuclei. These nuclei must be ones not found in the native coal otherwise their signals will be obscured. The candidates for such a nuclei are: ^{13}C, ^{19}F, ^{29}Si, ^{119}Sn, ^{31}P. These all have nuclear spin $I = \frac{1}{2}$ and so give sharp resonances.

Typical reactions used to introduce these nuclei are:



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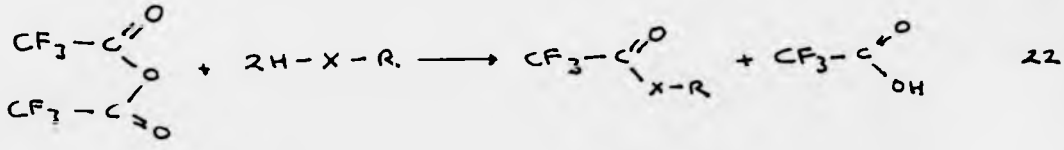

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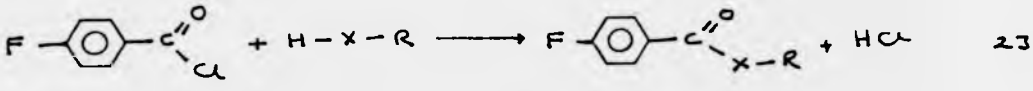

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$$[Si(CH_3)_3]_2NH + 2H\text{-}O\text{-}R \longrightarrow 2Si(CH_3)_3\text{-}OR + NH_3 \qquad 24$$

$$[Sn(CH_3)_3]_2O + 2H\text{-}O\text{-}R \longrightarrow 2Sn(CH_3)_3OR + H_2O \qquad 25$$

x = O,N,S

The nmr spectra of the introduced nuclei are recorded and used to infer the functional groups present. There are several properties one would wish the derivatization procedure to have. These include[26]

(i) The chemical shifts of the observed nuclei should be dispersed over a wide range of frequencies.

(ii) These shifts should be such that only one type of functionality gives a resonance in any one region of the spectrum.

(iii) The chemical shifts would ideally be related to the structure around the functional group in a simple and predictable manner.

(iv) The derivatization reaction should be quantitative so that the method can be used to determine the relative quantities of each group present.

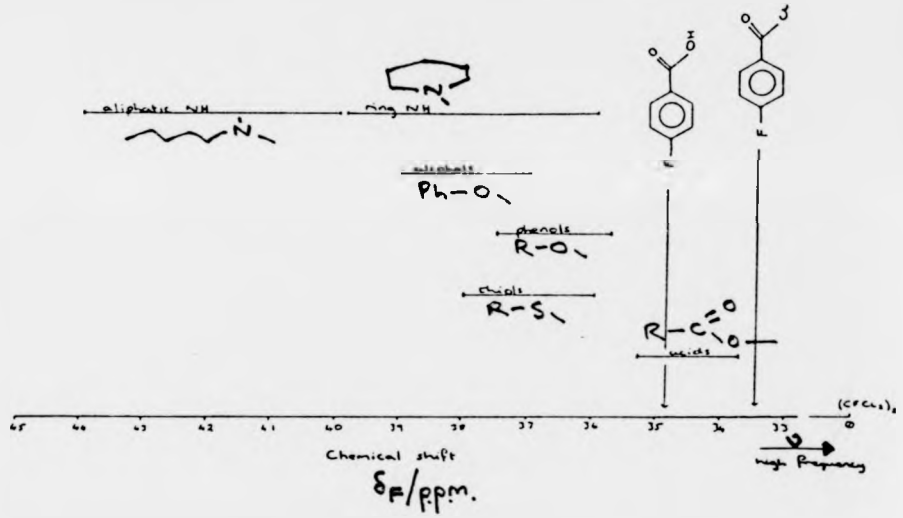
(v) The nuclei introduced must be relatively sensitive so that many species are observed.

(vi) The reaction must be easy to perform as complex reactions often fail with coal samples.

(vii) Resonances must be independent of concentration.

Not surprisingly none of the methods we investigated exhibited all of the above features. Initially fluorine seemed to be the most promising nuclei to use since it is very easy to observe and has a huge chemical shift range. We decided to try and follow up the work of Dorn et al [26,27] and use p-fluorobenzoyl chloride as a derivatizing agent. This is superior to hexafluoroacetone in that it is supposed to react more completely with hindered phenols, and has a larger shift range (10 ppm) than hexafluoroacetic anhydride. Using the WH 90 Spectrometer at Warwick we added to Dorn's list of Standards[27] and produced the following diagram of the chemical shifts of various derivatized groups:

^{19}F CHEMICAL SHIFTS OF o-FLUOROBENZOYL CHLORIDE DERIVATIVES

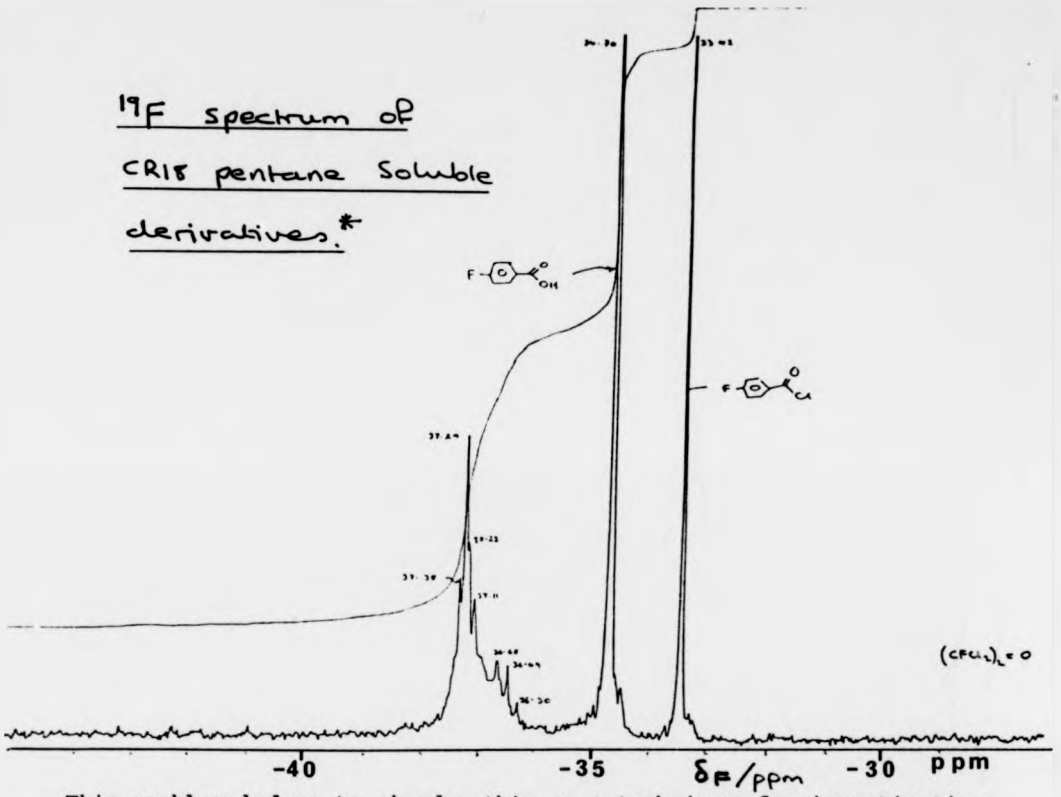


This diagram has two important features

(i) The reagent's ^{19}F resonance interferes with that of carboxylic acid derivatives.

(ii) phenol and amine derivatives are coincident.

The second feature is not a serious problem as these components may be separated by ion exchange chromatography (section 2.3). However (i) is a serious problem as the ^{19}F spectrum of a derivatized supercritical extract sample shows



This problem led us to abandon this as a technique for investigating the variation of functional groups. There were also considerable technical problems associated with the nmr instrumentation. Our search for a good derivatization technique led us to try trimethyl tin derivatives as reported by Rafii[25] but these were found to have highly solvent- and concentration-dependent resonances and therefore were no use for our purposes.

Eventually we settled for using trimethyl silyl derivatives, as these fulfill all the requirements mentioned above with the possible exception of sensitivity. But this can be overcome by using a high field instrument and modern pulse sequences. The use of silicon to study hydroxyl groups in coal tars and extracts forms the first part of our investigations into coal structure described below.

* see pages 75 and 146 for details of this extract

2. RESULTS OF SILICON DERIVATIZATION WORK

2.1 INTRODUCTION

The most abundant heteroatom in coal is oxygen. This is believed to exist principally as hydroxyl functionalities. We were interested therefore to know the exact nature of these groups and their relative abundance. As the hydroxyl protons are not well resolved in the ^1H NMR spectra of coal products, and these protons are easily replaced by other groups, this seemed an ideal problem for a derivatization approach. By converting the hydroxyl groups to trimethyl-siloxyl groups and observing the silicon NMR spectrum we were able to determine the proportions of hydroxyl functionalities in coal tars and extracts. By investigating the nature of these high yield solvent extracts and a rank series of low temperature coal tars with this technique, one can learn something about the nature of coal and how coalification proceeds. The formation of trimethylsilyl derivatives is a particularly good method for the following reasons:-

1) the derivatizations can be performed in an NMR tube by reaction of the sample with Hexamethyldisilazane(H.M.D.S.),

$$2R\text{-}OH + [Si(CH_3)_3]_2NH \longrightarrow 2ROSi(CH_3)_3 + NH_3 \quad ,$$

2) the silyl group tends to solublize hydrogen bonded material

3) no silicon is found in coal tars and extracts so no interfering signals are seen

4) the Chemical Shift range of trimethyl silyl groups is large and so many different species may be differentiated. In particular the reagents used do not resonate at the

frequency of the hydroxyl derivatives.

5) the silicon Chemical Shifts are insensitive to concentration and other solutes. The shift of benzoic acid in the CR18 benzene insoluble is exactly that found when it is recorded as a standard.

The only disadvantage of observing silicon NMR is that it is a relatively insensitive technique. This can be overcome by using polarization transfer techniques where the magnetization of coupled protons is used to excite the silicon nuclei. This works particularly well in this case as there are nine coupled protons to work with. Using this technique for silicon means one can detect 0.5 μmoles of an acid, phenol or alcohol. This is sufficient to get a good silicon-derivative spectrum of a coal tar or extract in about 12 hours.

2.2 PREVIOUS WORK

The use of hexamethyldisilazane to derivatize hydroxyl groups in coal products was first reported by Schweighardt et al in 1978.[28] This paper showed that the chemical derivatization procedure was effective over a wide range of different hydroxyl groups. The derivatives were investigated by ^{1}H.N.M.R. only. This gave ill defined spectra due to the small chemical shift range (about 100 Hz) of the various trimethyl silyl groups. However he did show that the reaction was quantitative for alcohols, phenols and carboxylic acids. The derivatives were first observed by ^{29}Si N.M.R. by Coleman and Boyd.[29] They recorded the ^{29}Si derivative spectrum of a coal asphaltene using the inverse gated decoupling technique. The sensitivity of this experiment is poor and little was observed. However this was improved upon by Dereppe and Parboo[30] in 1986 who implemented the I.N.E.P.T.[31] experiment

for silicon and thereby got a large increase in signal to noise. Unfortunately they had no accurate chemical shift data available and interpreted their spectra, recorded in deutero-chloroform, with the data of Coleman and Boyd which was measured using pyridine as a solvent.[29]

The most detailed work on silicon Chemical Shifts in silanes and siloxanes has been done by Schraml and Coworkers.[32] Their work involved the recording of spectra of pure liquids. These shifts are not useful for derivatization work except to illustrate the large shift range of trimethylsilyl derivatives. The 1981 paper of Schraml[32] shows how the chemical shifts of several series of silanes can be correlated with the Taft polar constant of a substituent group on silicon. These are equivalent to the correlations between chemical shift and pKa described below. The state of the technique before our work may be summarized as follows:

The silylation reaction was known to be quantitative and the silicon introduced observable by silicon N.M.R. using INEPT. The chemical shifts were known to be well dispersed and to show predictable trends with the polarity of substituents; a table of Shifts in deuterochloroform was not available.

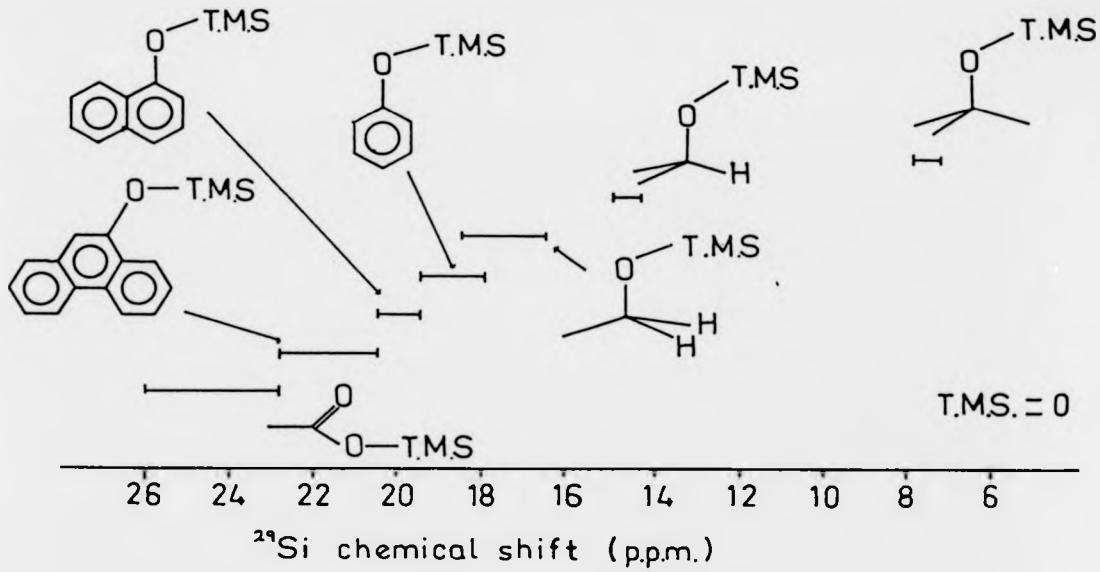
The technique had only been used for isolated samples and not for a rank series of coal products or a complete set of solvent extracts.

2.3 THE CHEMICAL SHIFTS OF SILYL-DERIVATIVES

In order that the technique be successful one must be able to interpret all the resonances or groups of resonances in the silicon spectrum. This can only be done once the chemical shifts of a large number of standards are known. A list of over 50 such shifts is given in

Appendix 2iii, these were recorded as described in the experimental section.

An examination of these shifts will show that the various hydroxyl functions are found in the regions indicated below.



The most important feature of the chemical shifts of the derivatives is that the alcohols, phenols and carboxylic acids are well separated; the only region of doubt being around 18 ppm. This turns out not to be a severe problem because the resonances of primary alcohols are concentrated at 17.0 ppm and the only phenols of such shifts are stericly hindered, e.g. σ-t-butyl phenol. In the absence of steric problems the chemical shift of a derivative will depend on the acidity of the corresponding hydroxyl group. Tertiary alcohols give a small shift whereas carboxylic acids give a large shift. Figures 4 & 5 show that for acids and phenols this relationship between acidity and

Figure 4

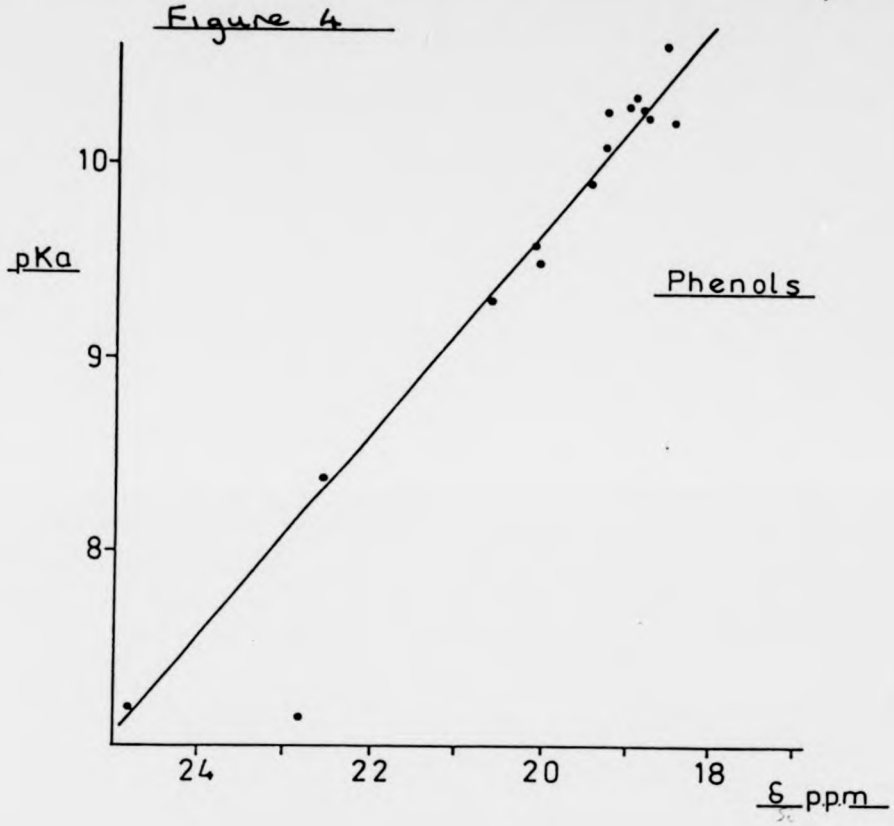
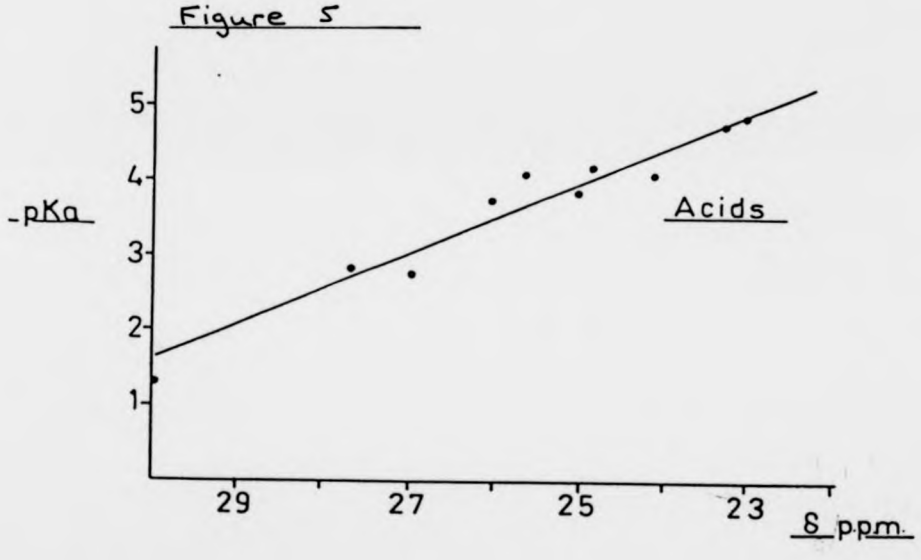
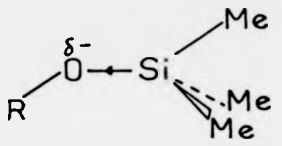


Figure 5



chemical shift is linear in the absence of steric hindrance at oxygen.

$$R\text{-}OH + H_2O \rightleftharpoons R\text{-}O^- + H_3O^+ \quad \underline{\underline{pKa}}$$



The silicon chemical shift is monitoring the polarization of the silicon oxygen bond. If R is electron-withdrawing then the polarization will be large and hence so will the chemical shift. The acidity of a phenol depends on the stability of its anion, this also depends on the electron withdrawing power of R. Therefore one would expect that the two quantities pKa and chemical shift would be related; although not necessarily in a linear fashion. Sterically hindered phenols fall to the right of the line in diagram 4 . In this case the relationship breaks down as there is a contribution to chemical shift independent of the bonding in the system.[33]

Having established this relationship between chemical shifts and acidities one may separate the phenolics into three distinct groups; phenols, napthols and polyaromatic phenols. These assignments can only be made in the absence of electronegative groups on the phenols, as is the case in many coal tar samples. When

32

there is doubt about the nature of components at δ = 22 ppm they are referred to as "higher phenols" in order to recognize the possible ambiguity.

On the basis of the extensive list of standards recorded and the correlations with acidity we have considerable confidence in the interpretation of the coal tar and solvent extract derivative spectra presented below.

2.4 DISTRIBUTION OF HYDROXYL FUNCTIONS IN A SUPERCRITICAL SOLVENT EXTRACT CR 18 *

The discussion above shows that using silyl derivatives to determine hydroxyl functions in coal is a good technique in that the derivatives resonate over a large range of frequencies and that these shifts are easily explained. In order to investigate the functionalities in coal one must get them into solution. One method that is believed to do relatively little damage to the coal structure is that of supercritical extraction at 420°C with toluene.[34] This produces an extract representing 35% of the original coal. For the purposes of analysis this material is then fractionated into:-

Pentane solubles 33%

Asphaltenes (Pentane insoluble/Benzene Soluble) 33%

Benzene Insolubles 33%

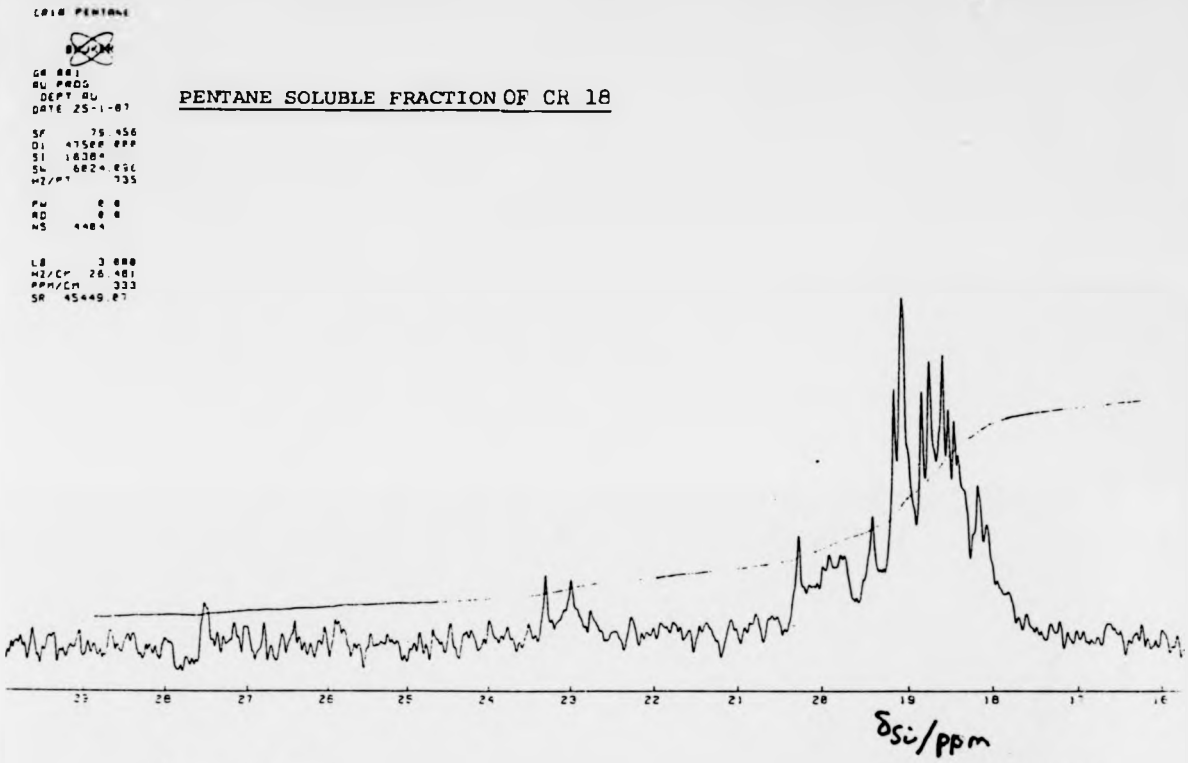
The advantage of this procedure is that the 3 fractions have very different average molecular masses and so one can see how the nature of hydroxyl groups in the extract varies with the average molecular mass. This may tell us if the small molecules are simply subunits of the larger molecules or are fundamentally different. A detailed description of the hydroxyl groups in these fractions is given below. The relative abundance of acids, phenols and alcohols are shown in table 2.

* Analysis of this material is given in Appendix 2(i) p.146.

SUPERCRITICAL EXTRACTS Table 2

	acids %	higher phenols %	napthols %	phenols %	alcohols %
pentane solubles	8	8	16	68	-
asphaltenes	12	19	38	31	
benzene insolubles	16	27	37	20	-
pentane sol acids	14	12	43	31	-
asphaltene acids	20	27	37	20	-

The figures represent the proportion of each functionality as a % of total hydroxyl content.



PENTANE SOLUBLE FRACTION OF CR 18

δ = 23 ppm — CARBOXYLIC ACIDS

These two peaks are caused by straight chain aliphatic (fatty) acids.

δ = 20.75 - 23 ppm — "HIGHER PHENOLS"

The absence of any distinct resonances in this region of the ^{29}Si derivative spectrum shows that there are few polyaromatic phenols or very acidic phenols present in this sample.

δ = 19.5 - 20.75 ppm — NAPTHOLS

The prominent peak at 20.2 ppm is probably 2-Napthol. The peaks to the right of this are methyl and dimethyl 2-Napthols.

δ = 17.5 - 19.5 ppm — PHENOLS

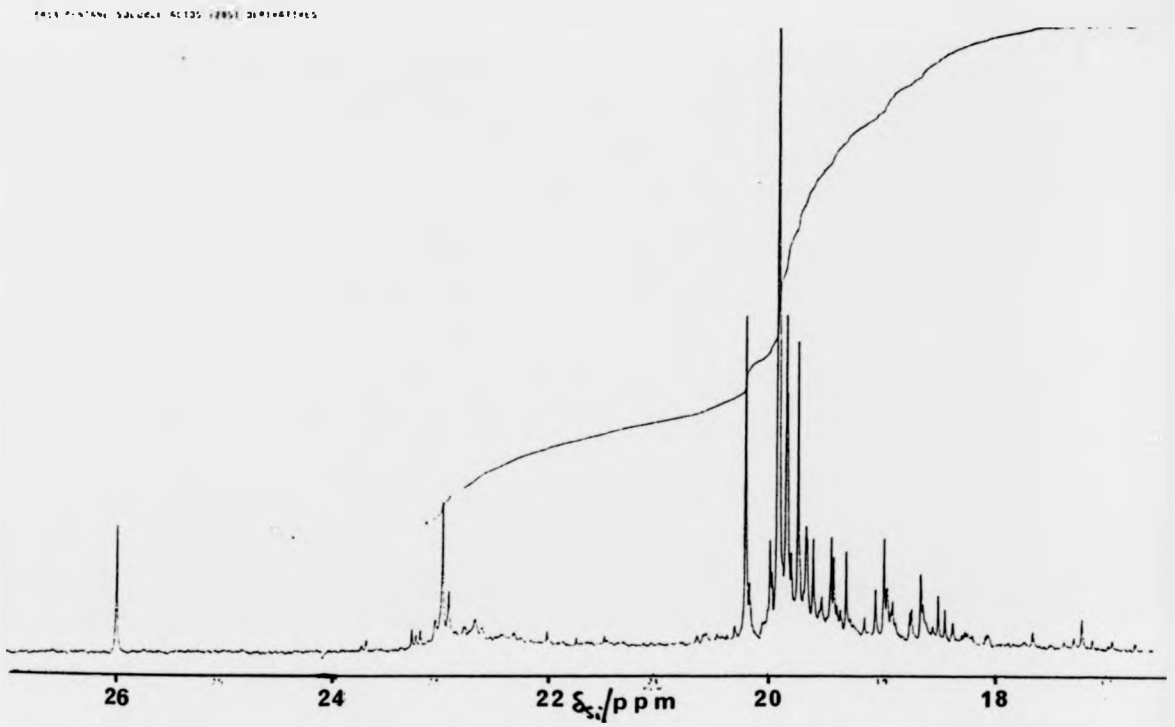
There is a small peak at δ = 19.4 ppm due to phenol itself. δ = 19.1 are cresols and the bond δ = 18.9 - 18.4 ppm Xylenols. The remaining resonances are due to

alkyl chains at the 2-position of phenols or trimethyl phenols.

δ = 17.5 ppm ALCOHOLS

These are not observed in this sample.

PENTANE SOLUBLE ACIDS OF CR 18



The phenolic and acidic components of the pentane soluble fraction were concentrated by ion exchange chromatography. The ^{29}Si derivative spectrum of this sample is described below:

δ = 23 ppm "FATTY" ACIDS

δ = 20.75 ppm - 23 ppm "HIGHER PHENOLS"

This is a featureless band even

after concentration of the acidic components by chromatography. To distinguish between polyaromatic phenols and phenols containing electron-withdrawing substituents we must turn to the ^{1}H NMR spectrum of this material. This shows an aromatic band extending to 8.0 ppm indicative of polyaromatic phenols rather than single ring material.

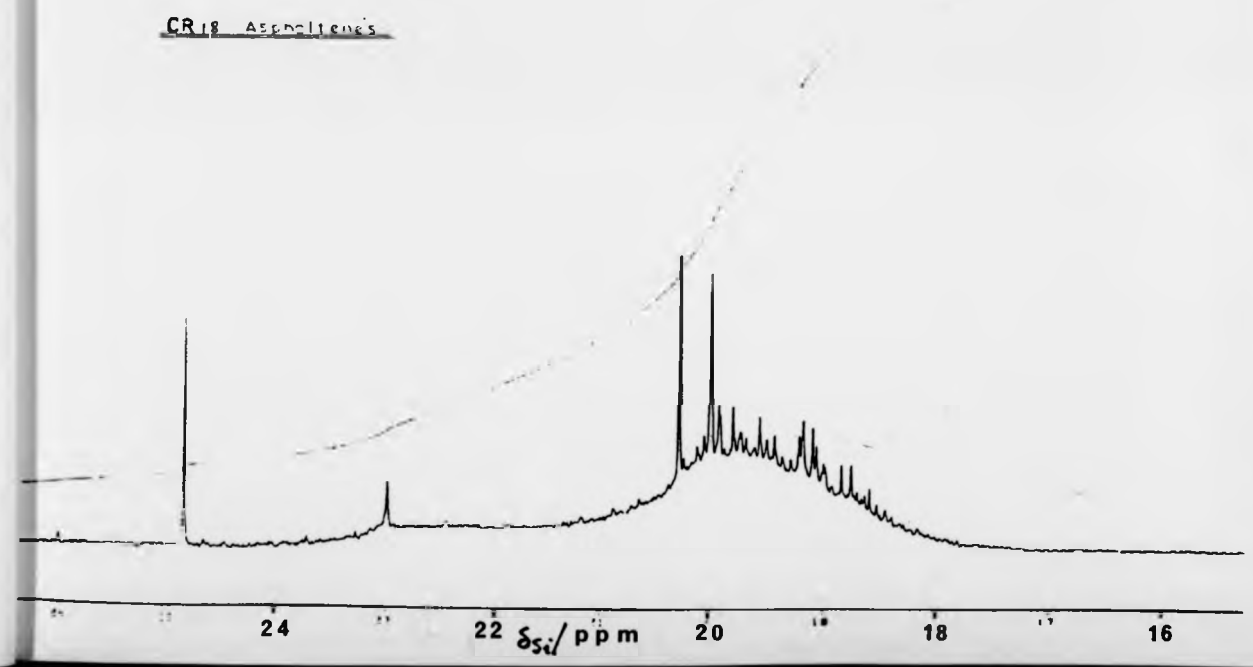
δ = 19.5 ppm - 20.75 ppm NAPTHOLS

The dominant species are 2-napthol and methyl/dimethyl 2-napthols. Only a tract of 1-napthol and methylated analogues are observed.

δ = 17.0 ppm - 19.5 ppm PHENOLS

These are not as abundant as the napthols. This is due to the chromatography which selects the more acidic species. The phenols present are all alkylated, some to a large degree δ = 17.25. No individual component is dominant.

ASPHALTENES



The outstanding feature of this sample is the enormous number of different species present.

δ = 23 ppm "FATTY ACIDS"

δ = 20.75 - 23 ppm "HIGHER PHENOLS"

These are polyaromatic phenols as shown by the ^{1}H spectrum. This has an aromatic band extending up to 9.0 ppm. This is as expected for a sample of much greater average molecular mass than the pentane solubles.

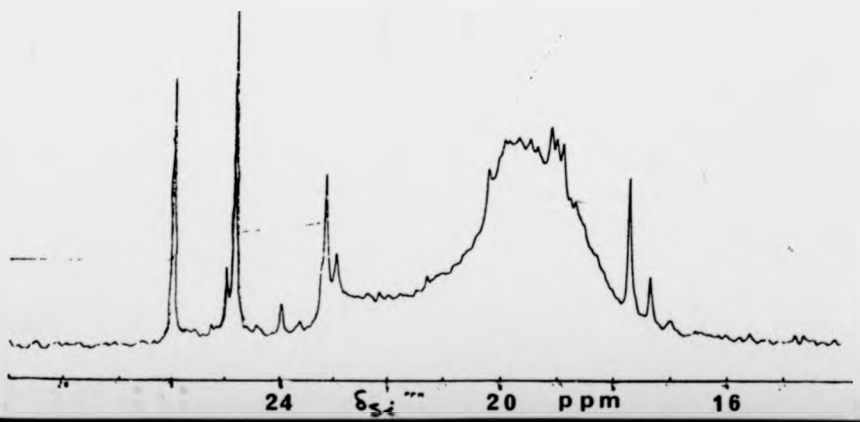
δ = 19.5 ppm - 20.75 NAPTHOLS

Dominant species are 2-napthol and a methyl 2 napthol

δ = 17.5 - 19.5 ppm PHENOLS

Again we have no dominant species. The observation that almost all conceivable alkylated phenols are present is consistent with the known very high oxygen content of this material. (See Appendix 2(i).)

ASPHALTENE ACIDS OF CR 18

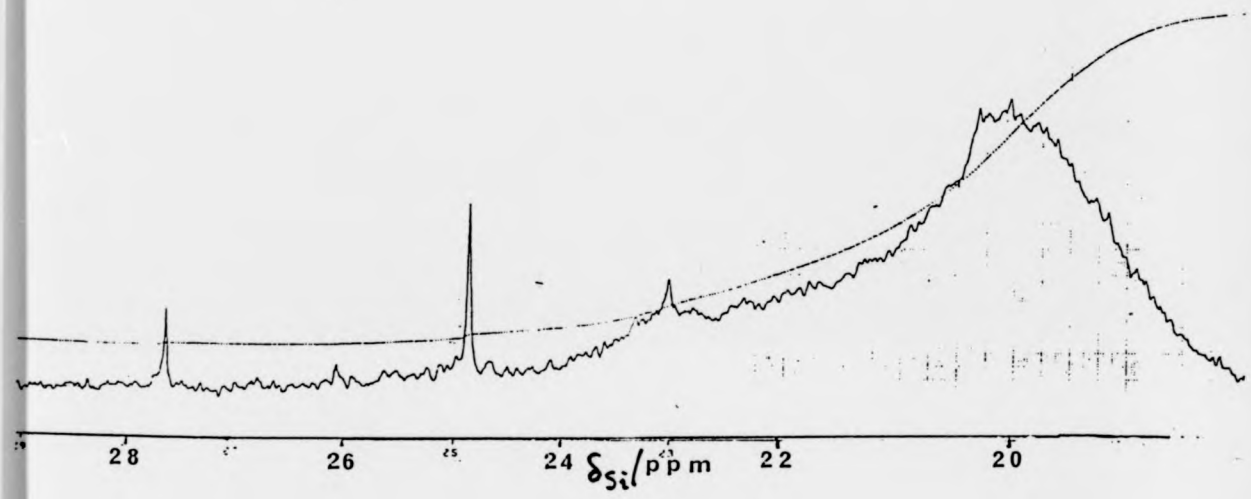


In addition to the broad spectrum observed for the total asphaltenes, the acids have brought out the following features:

δ = 26.0 ppm	formic acid from the extraction process.
δ = 25 ppm	Benzoic type carboxylic acids. These were not observed in any other coal product looked at by us.
δ = 23 ppm	enhanced fatty acid peak.
δ = 17 - 18 ppm	?

BENZENE INSOLUBLES

CR18 Benzene insolubles



2.5 DISCUSSION OF THE ^{29}Si SPECTRA OF SUPERCRITICAL EXTRACT FRACTIONS

The supercritical extraction process using toluene produces an extract that represents 35% of the original coal. It is not possible to make any statements regarding the other 65% on the basis of ^{29}silicon derivative spectra alone. The extract contains all the material not bound strongly to the polymeric material of the coal. Although heated to only 450^{o}C some chemical change has occured. This is clear from the molecular mass of the extract as compared with that found for soxhlet extractions. However it is unlikely that such a temperature has affected the aromatic units in the coal.

These samples show two discernible trends as the average molecular weight increases:-

1) The spectra became dominated by broad bands rather than individual peaks. This indicates that more components are present in the heavier materials. This is due to the larger number of isomers possible for larger molecules.
2) As the fractions and molecular weights increase the "higher phenol" bands become more intense and the phenols less intense.

   Again this is as expected but it is interesting to note that the proportion of phenolics that are either napthols or single ring phenols is as high as 70% for the unfractionated extract.

   This is an important observation as the average molecular mass of this material ~600 Daltons, but the mass of a napthol is 144. From the elemental analysis of CR18 we know that on average each molecule contains 2 or 3 oxygen atoms. So we must think of the supercritical extract,

and by inference the mobile phase of coal, to be oligomeric in nature, and made up of several aromatic systems united together in some way. We SPECULATE that the insoluble material is in part similar to these oligomers. However they are heavily cross linked and therefore inaccessible to supercritical solvent extraction.

2.6 DISTRIBUTION OF HYDROXYL GROUPS IN COAL TARS

The coal tars used in this study were 600°C distillation products of a range of British and overseas coals and coal precursors. (see table 3) These coals form a rank series. Their carbon content ranges from 50 to 93%. The basic assumption is that these materials are representative of one coal in different stages of coalification from wood and peat through lignites and finishing with high rank bituminous coals or anthracites. This is clearly a gross oversimplification but one must start somewhere. This assumption is found wanting most noticibly with the turkish tar. Although this material follows the reproducible features and trends found for the rank series its silicon derivative spectrum is remarkably simple. This may be in part due to the coal being geologically heated to a higher temperature than the other materials. However simplification of spectra is a major trend for the low rank tar materials.

The general separation of hydroxyl groups into acids, phenols and alcohols is shown in figure 6 , and what appears below is a more detailed description. Proton NMR spectra were recorded for each sample and were used to clarify certain ambiguities in the silicon spectra.

Table 3

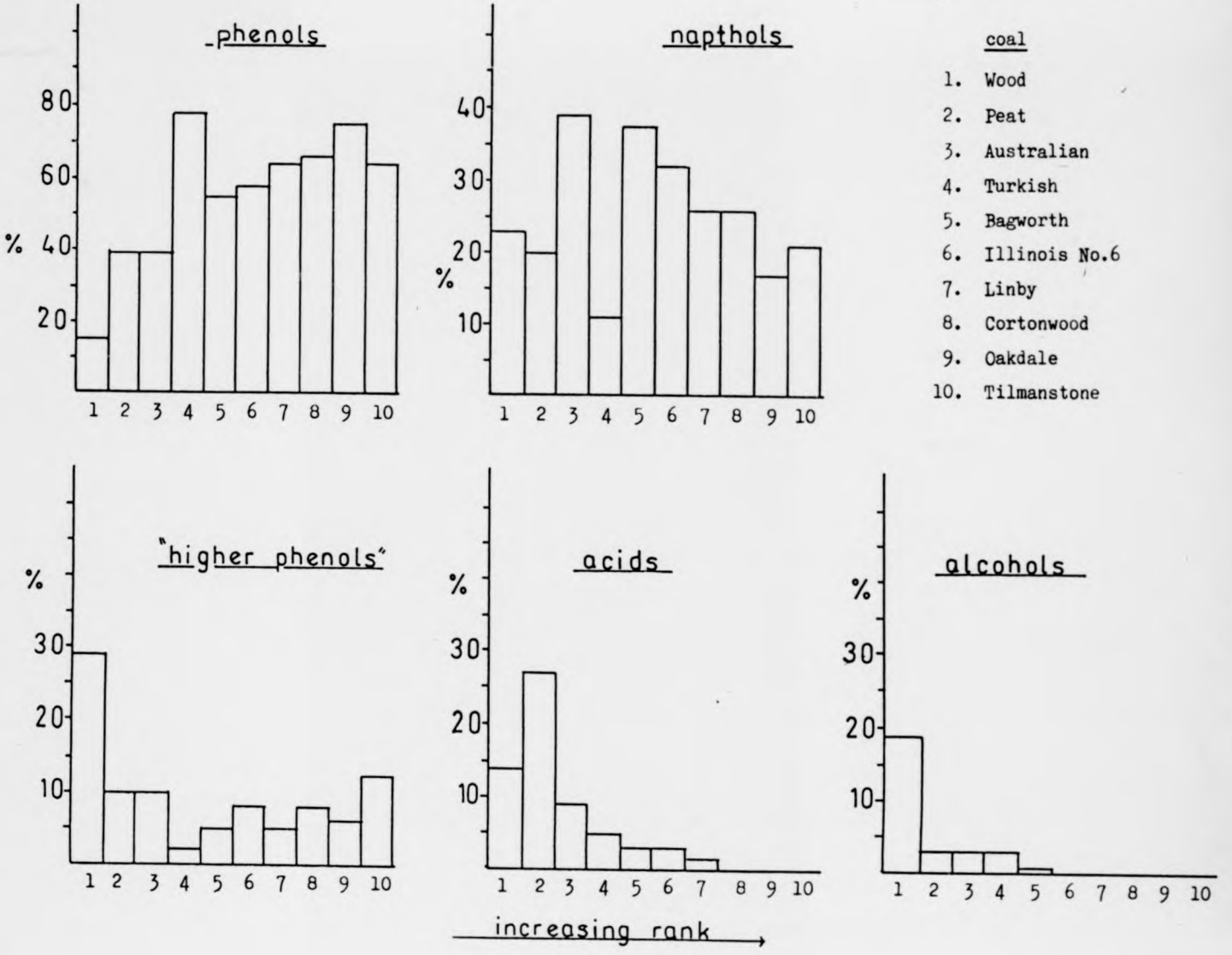
IMPORTANT COAL DATA

	% C dmmf	% O dmmf	% tar ad	Total volatile daf*
Tilmanstone	92.40	2.00	2.4	17.0
Oakdale	90.5	2.40	2.74	21.5
Cortonwood	87.20	3.9	9.64	35.8
Linby	83.00	8.70	6.17	37.9
Illinois No. 6	82.50	8.8	16.79	45.9
Bagworth	80.60	11.30	10.02	43.3
Turkish	74.80	14.52	3.79	57.8
Australian LV1276	66.90	26.30	3.56	50.4
Peat	59.50	32.30	14.35	70.2
Wood	50.80	42.70	31.23	84.3

* See abbreviations p.7.

Figure 6

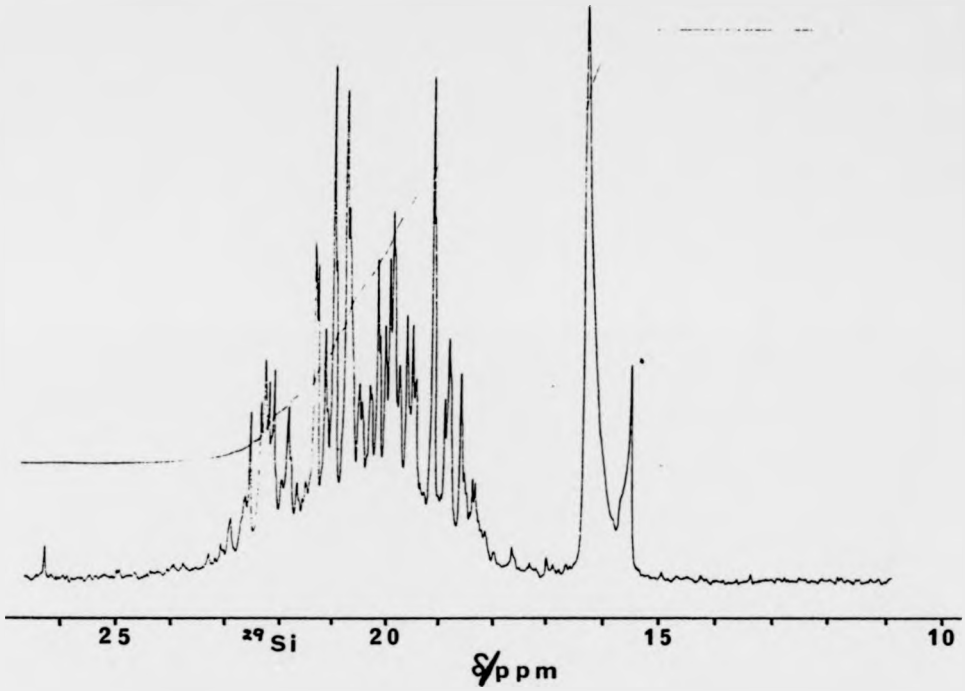
HISTAGRAM SHOWING THE DISTRIBUTION OF HYDROXYL FUNCTIONS IN TEN COAL TARS ARRANGED ACCORDING TO COAL RANK.



coal

1. Wood
2. Peat
3. Australian
4. Turkish
5. Bagworth
6. Illinois No.6
7. Linby
8. Cortonwood
9. Oakdale
10. Tilmanstone

WOOD TAR



From the spectrum it is clear that there is a wide variety of each type of hydroxyl functionality.

δ = 22.5 ppm - 25 ppm CARBOXYLIC ACIDS

These are mostly (80%) straight chain aliphatic (fatty) acids. Those resonances appearing above 23.5 ppm being due to more acidic species.

δ = 20.75 ppm - 22.5 ppm "HIGHER PHENOLS"

These resonances are due to the presence of very acidic phenols.

For this sample it is clear from the ^1H spectrum that these are single-ring phenols or napthols with electron-withdrawing substituents, rather than polyaromatic phenols. The ^1H spectrum shows few resonances $\gtrsim$ 8.0 ppm but many due to aromatic protons between 7 and

44

6 ppm. It also has a large resonance at δ = 3.8 ppm due to aryl-methyl ethers, these methoxy groups significantly increase the ^{29}Si chemical shift of phenol derivatives.

δ = 19.5 ppm - 20.75 ppm NAPTHOLS

In this region one can see a resonance corresponding to 1-napthol (δ = 20.57). The rest of the resonances however are difficult to assign and are probably due to single-ring phenols with electron-withdrawing substituents.

δ = 17.5 ppm - 19.5 ppm PHENOLS

The "normal" phenolic region of the spectrum is very simple showing only phenol δ = 19.41 ppm

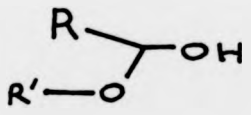
m, p cresols δ = 19.1 ppm

o- cresol δ = 18.8 ppm

and a small amount of xylenols. The methyl resonances of these species are very prominent in the ^{1}H spectrum. However it is clear that CH_3 - Ar groups are found also in the more acidic species.

δ = 16.31 ppm and = 15.35 ppm ALCOHOLS

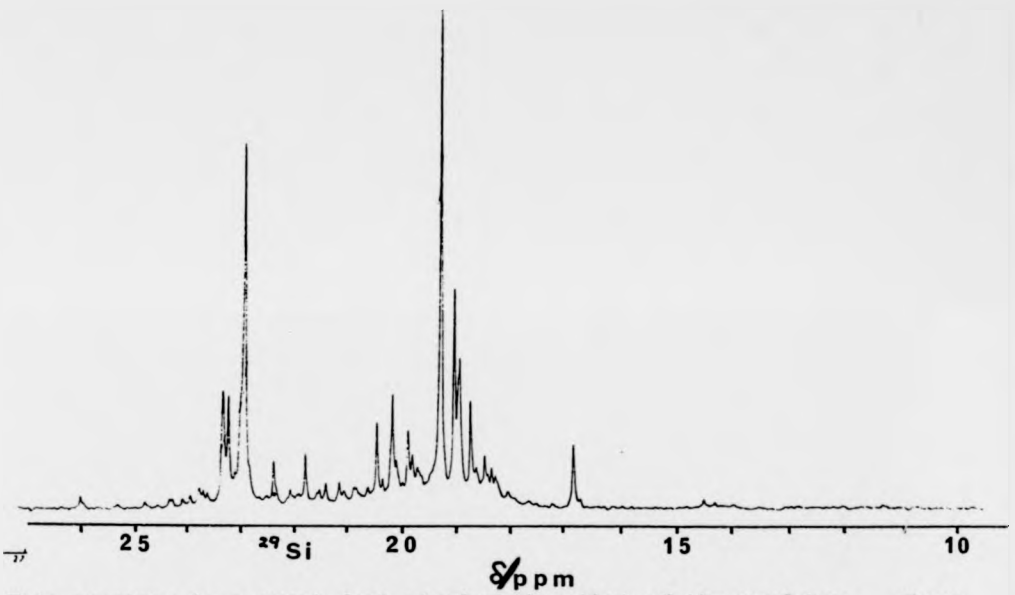
The chemical shifts of both these species are well below that found for primary alcohols. Therefore they are probably secondary alcohols of the type



such species might be formed from the pyrolysis of cellulose. *

* See p.58.

PEAT TAR



This spectrum is a great deal simpler than that of the wood tar. There are many fewer species particularly of the more acidic type

δ = 22.5 ppm - 25 ppm CARBOXYLIC ACIDS

The large peaks at 23 ppm are caused by fatty acids those above 23.5 ppm by more acidic species.

δ = 20.75 ppm - 22.5 "HIGHER PHENOLS"

The important feature to note about these is that they are due to the same species as in the wood tar. However there are far fewer of them.

δ = 19.5 ppm - 20.75 ppm NAPTHOLS

Again 1-napthol at δ = 20.57 ppm is the most obvious feature. The two other major peaks are probably 2-napthol and methyl 2-napthol derivatives.

δ = 17.5 - 19.5 ppm

PHENOLS

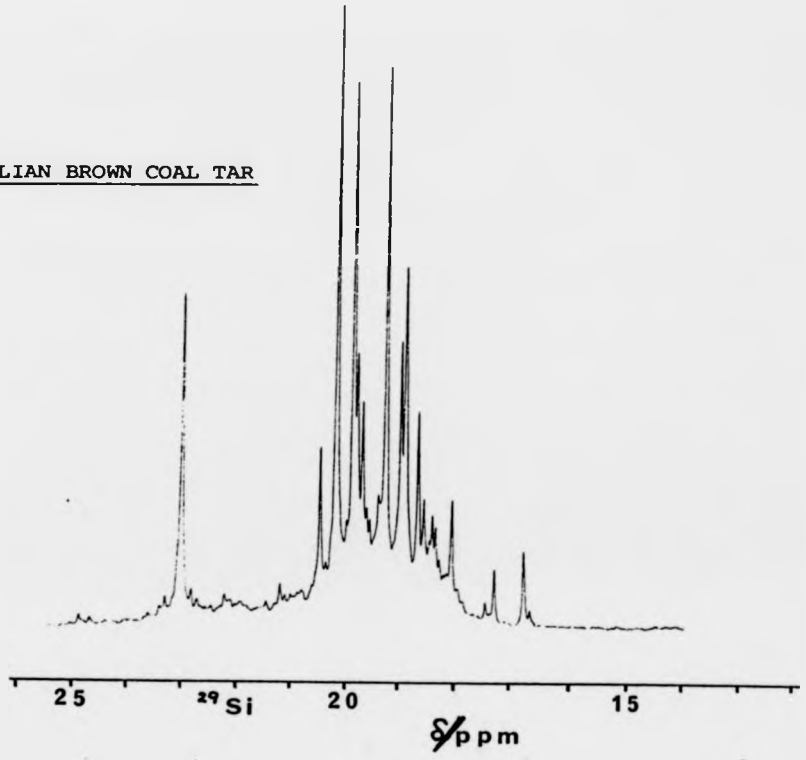
These are virtually identical to those of the wood tar with phenol and the cresols being the dominant species.

δ = 16.87 ppm

ALCOHOLS

This resonance represents many different alcohols but all primary and probably of the form

AUSTRALIAN BROWN COAL TAR



δ = 22.92 ppm

Fatty acids are virtually the only type of carboxylic acid present in this tar.

δ = 20.75 - 22.5 ppm "HIGHER PHENOLS"

These are the same species as found in the peat tar. However it is possible from the ^1H spectrum that some polyaromatic phenols are present. In any event the intensity of this band is very low and is not a significant feature in the spectrum.

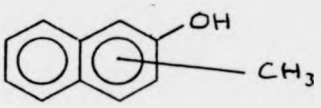
δ = 19.5 ppm - 20.75 ppm NAPTHOLS

This region is dominated by just a few species. A possible interpretation of these signals is:

major peaks

δ = 20.2 ppm 2-napthol

minor peaks δ = 19.9 ppm, 19.8 ppm, 19.7 ppm



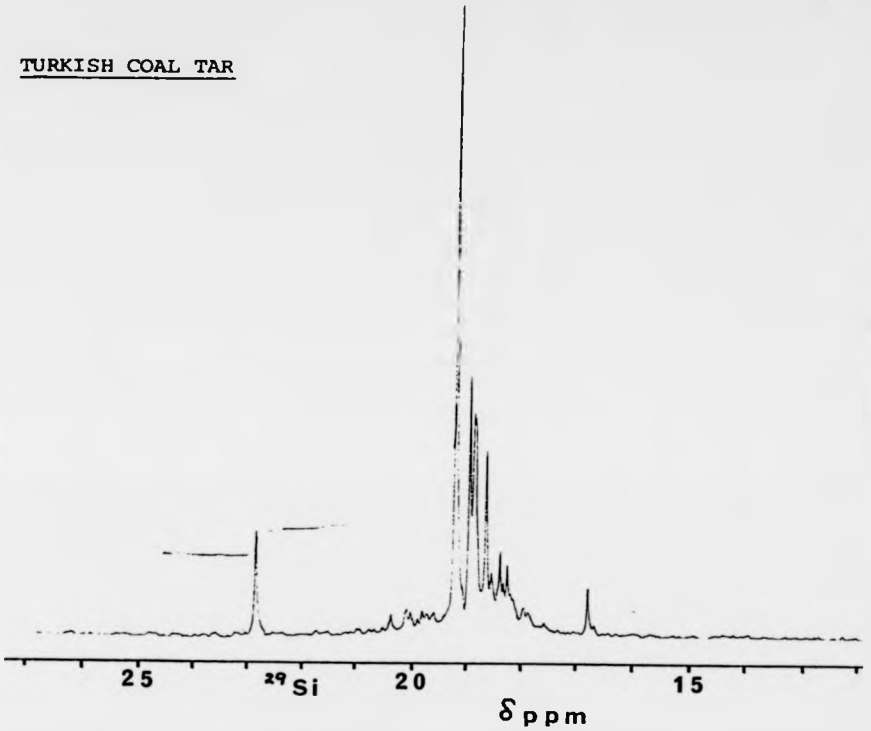
20.5 ppm 1-napthol

δ = 18.0 ppm - 19.5 ppm PHENOLS

In addition to those species observed in the peat tar there is a proportion of highly alkylated material δ = 18.0 - 18.4 ppm. This is probably caused by alkyl chains at the 2-position of phenol. From recording derivative spectra of such compounds we know they have lower chemical shifts than xylenols; although tri-methyl phenols are a possibility for these resonances.

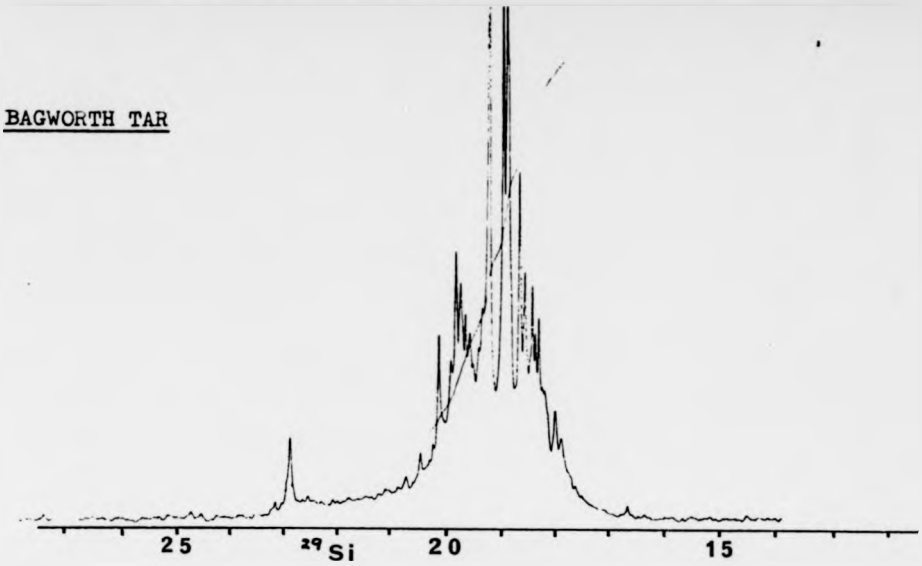
δ = 16.5 ppm - 17.5 ppm PRIMARY ALCOHOLS

TURKISH COAL TAR



The most striking feature of this spectrum is its simplicity. It is completely dominated by phenol, cresols and xylenols with few napthols and little or no "higher phenols". The alcohols and acids present are both simple straight chain alkyl compounds. This spectrum marks the end of a trend in the coalification process. Up to this point the spectra of the derivatized tars have simplified with increasing rank, but the remaining tars have a more varied composition.

BAGWORTH TAR



This is the first British coal of the series, and is a sub-bituminous coal rather than a true lignite.

δ = 23 ppm FATTY ACIDS

δ = 20.75 - 23 ppm "HIGHER PHENOLS"

This region is relatively featureless. It is caused by the presence of polyaromatic phenols. The presence of the very acidic single ring-phenols found in the wood tar can be discounted from on inspection of the proton NMR spectrum. This shows NO aryl-methyl ether and a broad aromatic band extending up to 8.0 ppm.

δ = 19.5 ppm - 20.75 ppm NAPTHOLS

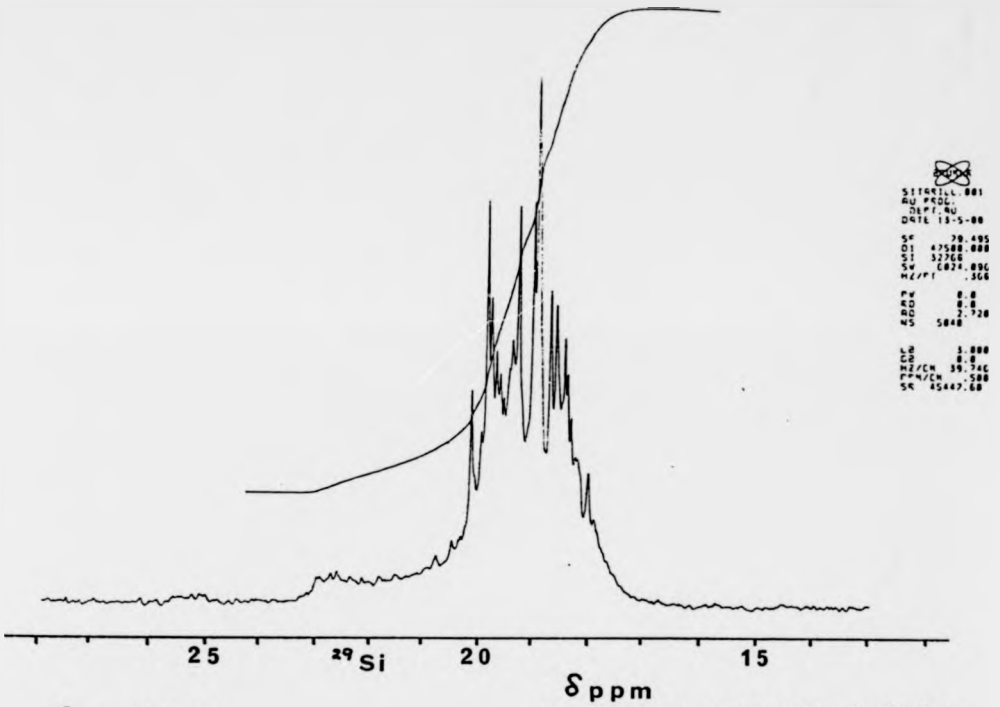
These are relatively easy to identify. There is only a trace of 1-napthol δ = 20.5 ppm with the majority of peaks being due to 2-napthol 20.2 ppm and methyl 2-napthols 19.5 ppm - 20 ppm.

δ = 17.0 ppm - 19.5 ppm PHENOLS

A similar band to that found in the turkish tar spectrum. The main difference being that more highly alkylated materials are present.

δ = 16.8 primary alcohols - a trace.

ILLINOIS # 6 TAR



δ = 23 ppm — No distinct resonances implying that there are no fatty acids in this sample

δ = 20.75 ppm - 23ppm — POLYAROMATIC PHENOLS

This broad band is characteristic of bituminous coal tars.

δ = 19.5 - 20.75 ppm — NAPTHOLS

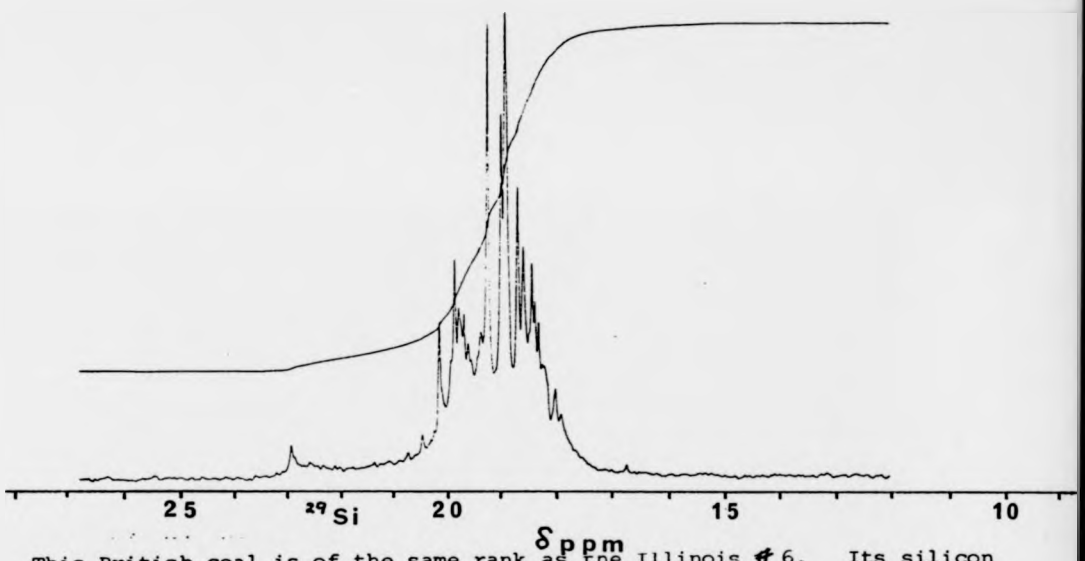
As for the Bagworth tar this region is dominated by 2-napthol and methyl 2-napthols. 1-napthol is almost completely absent.

δ = 17.0 ppm - 19.5 ppm — PHENOLS

In this sample the cresols are more abundant than phenol itself. In general the phenols in this sample are more alkylated than in the Bagworth tar.

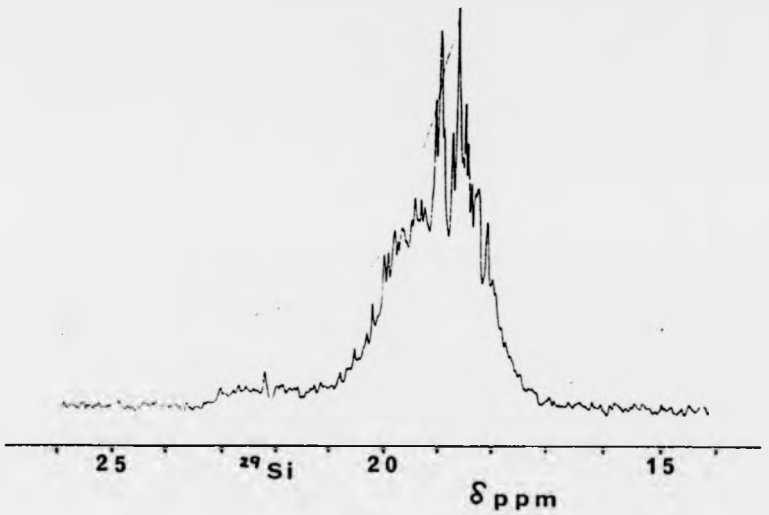
δ < 17 ppm — No alcohols

LINBY TAR



This British coal is of the same rank as the Illinois #6. Its silicon derivatized tar is of an almost identical composition as seen by ^{29}SiNMR, and ^{1}H NMR.

CORTONWOOD TAR



With coals of this rank the tars do not contain alcohols or carboxylic acids in significant quantities.

δ = 20.75 - 23 ppm POLYAROMATIC PHENOLS

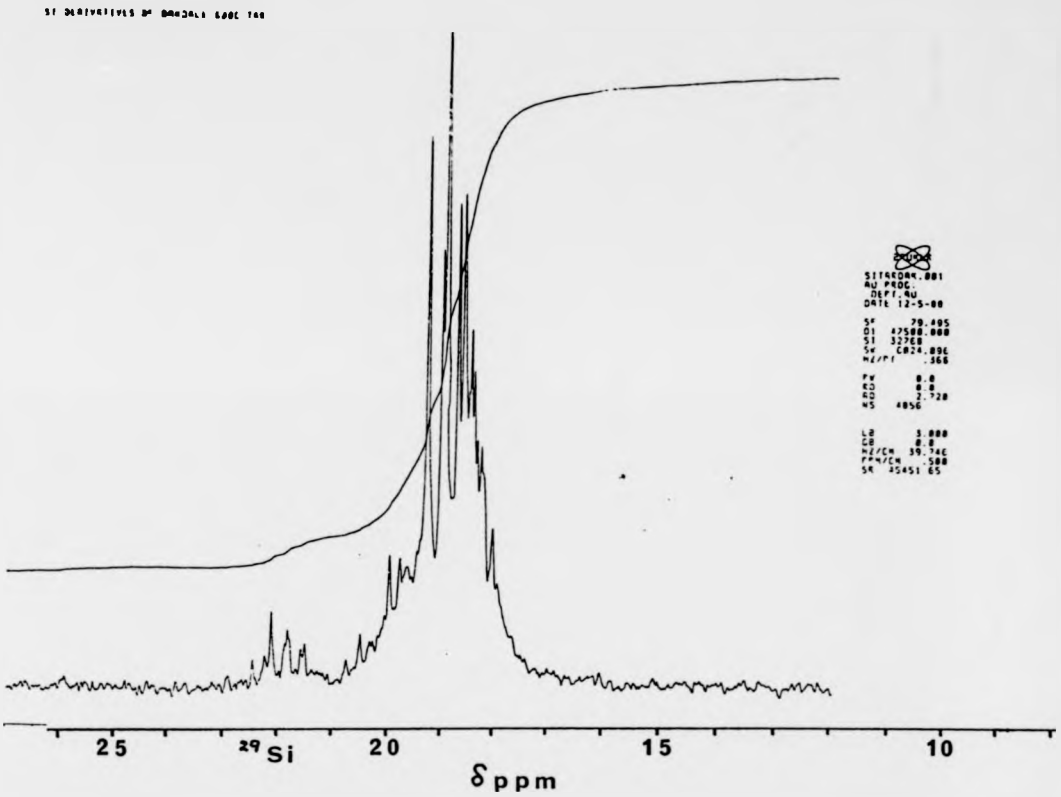
δ = 19.5 - 20.75 ppm NAPTHOLS

These are very heavily alkylated as shown by the very many peaks between 20 ppm and 19.5 ppm. Indeed it is probable that some peaks between 19.00 and 19.50 are napthols.

δ = 17.0 - 19.5 ppm PHENOLS

Like the napthols these are highly alkylated species. The cresols and xylenols being the dominant components.

OAKDALE TAR



This is a high rank British bituminous coal and as such one would expect its 600°C tar to contain some polyaromatic material.

δ = 20.75 - 23 ppm — POLYAROMATIC PHENOLS

Several individual species can be seen although they cannot be identified.

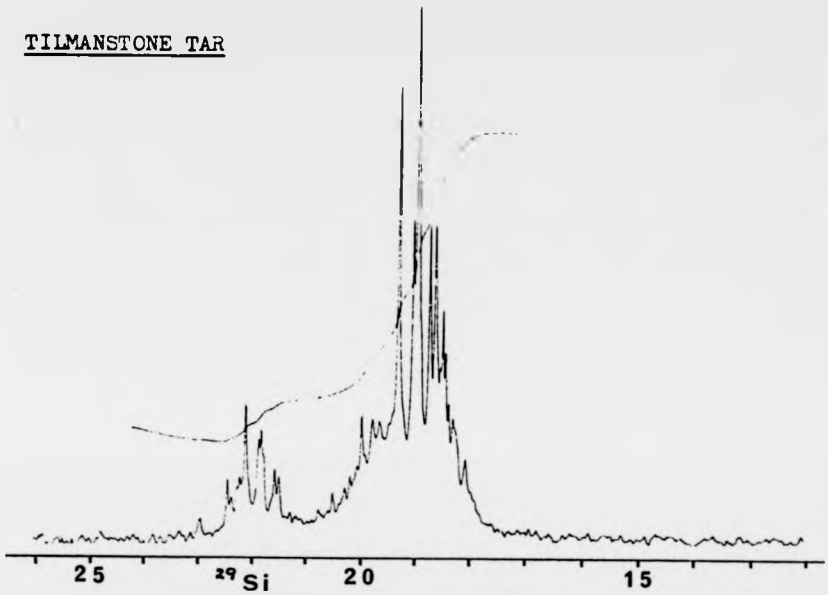
δ = 19.5 - 20.75 ppm — NAPTHOLS

Again these are highly alkylated. There are relatively fewer napthols in this sample than in the Cortonwood tar.

δ = 18.5 19.5 ppm — PHENOLS

These are very similar to those found in the Cortonwood tar. However the alkylation is not as heavy as shown by the lack of phenols 17.5 ppm.

TILMANSTONE TAR



This tar is very similar to the Oakdale tar. However the polyaromatic phenols are more pronounced, as expected.

2.7 DISCUSSION

In order to gain useful information about the nature of coal from these spectra it is essential to have some model for how the tars are formed. These tars were produced from a rank series of coals and coal precursors in order to determine if their composition was rank dependent.

The tars were produced in an oxygen free environment, so it is reasonable to assume that no oxidation occurs during pyrolysis and that the oxygen content of the tar comes from the coal itself. The important question is: from which parts of the coal does the tar come?

Solvent extraction studies have found that most of the coal structure is completely insoluble in any solvent at non-supercritical temperatures. This observation has led to the belief that coal is essentially a 3-D cross-linked polymer.[35] This insoluble polymer is surrounded by a phase

Figure 7

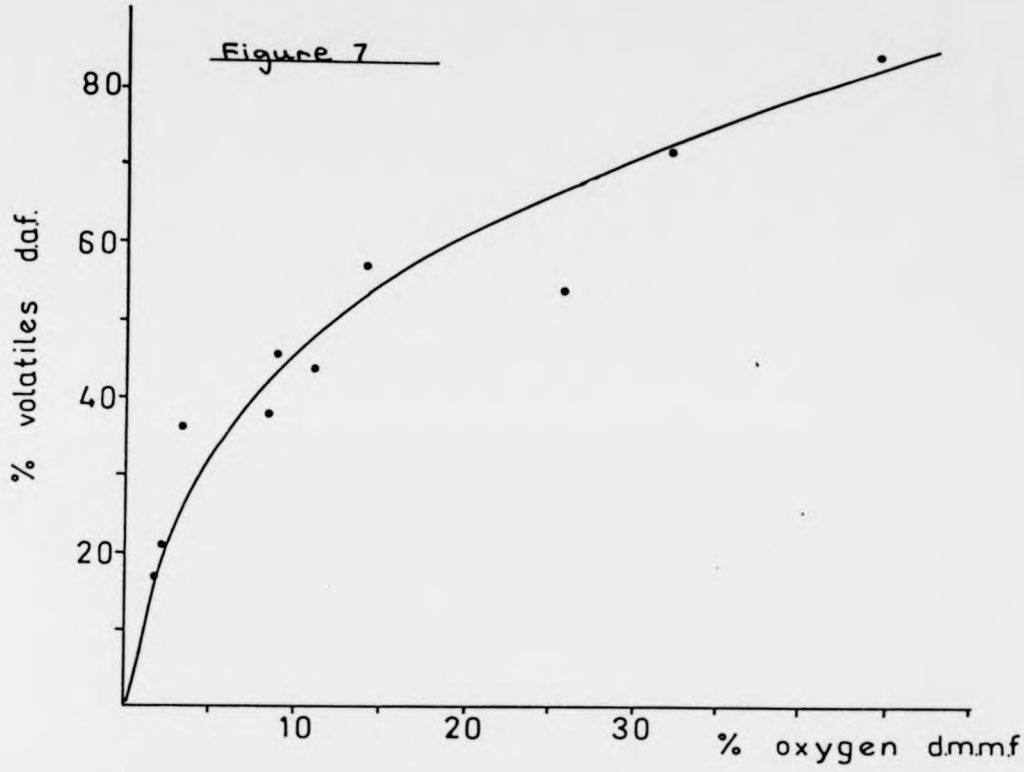


Figure 8

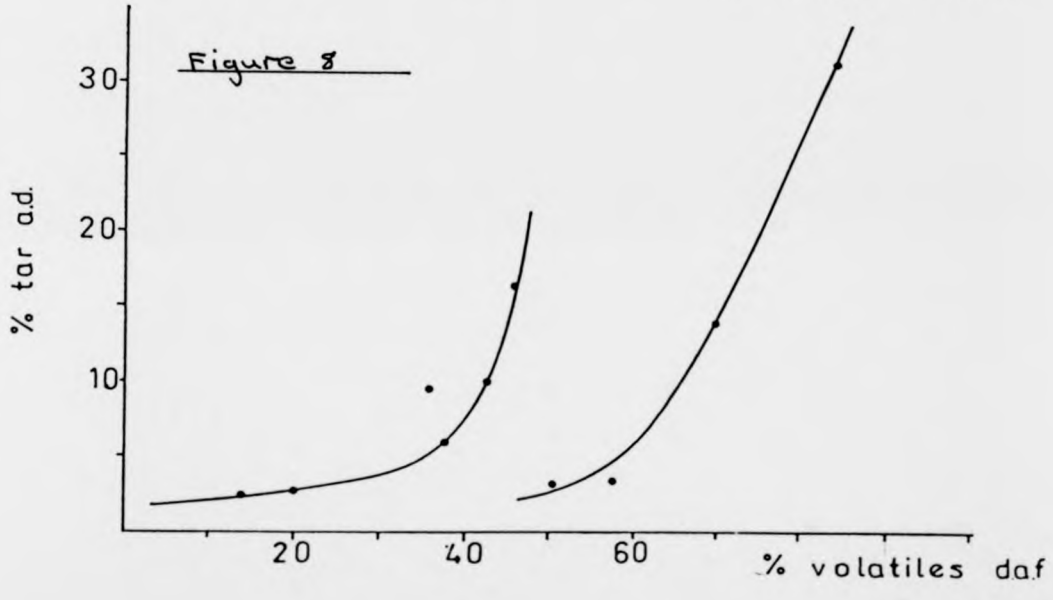
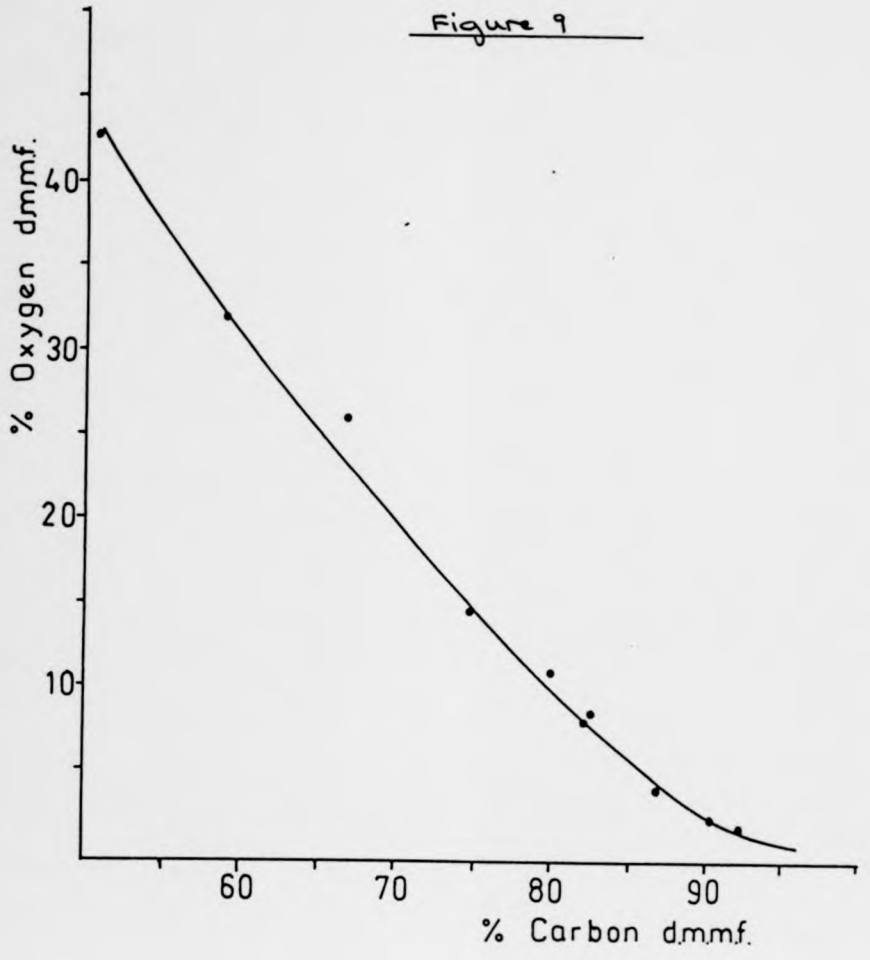


Figure 9



that may be extracted with suitable solvents, e.g. pyridine. This mobile phase has been the basis of many structural studies in the past.[36] Our studies with pyridine extractions indicate that this mobile phase is probably oligomeric in nature. It is very insoluble in most solvents, e.g. chloroform, and is not solubilized by silylation. Several groups have attempted to measure the relative molecular mass of such materials and have found values of between 1 and 2000 Daltons.[37] This mobile phase is not simply volatilized by 600°C pyrolysis, the tars produced are all soluble in chloroform whereas the solvent extracts are not. Also molecules with such large molecular masses as found in the mobile phase would be expected to decompose before vaporising. Thus the tars are pyrolysed, rather than purely vaporized, material produced under reducing conditions. The question now is, which functionalities in the coal are broken during pyrolysis?

It is interesting to note that the mass of total volatile products from tar production is related to the oxygen content of the original coal it was produced from. High oxygen content, and hence low rank, implies high volatiles, low oxygen implies low volatiles (see figure 7). This SUGGESTS that oxygen atoms are associated with the pyrolysis process. For example pyrolysis may cause the breakage of all "hydrogen bonds" and of many covalent carbon-oxygen bonds. The tars are part of the total volatiles, but do not constitute a fixed fraction of it as figure 8 shows. It can be seen from this that the materials fall into two groups; the bituminous coals, and lignites and coal precursors. The relative decrease in tar yield shows that the small side-chains responsible for the coal gases are not lost as fast during coalification, as the tar producing materials are "fixed" into the involatile coal structure. This "fixing" is probably due to the formation of more cross-links within the coal as it ages.

The discussion below on what happens during coalification is based on the following summary of what occurs during the 600°C pyrolysis.

1. The tar does not come from the mobile phase alone. However the greater proportion of it does. (see 4 below)
2. The oxygen in the tar came originally from the coal. However it may have been in a different form.
3. The tar consists of volatile molecules broken from larger oligomers and polymers by cleavage of H-bonds and C-O covalent bonds, (possibly C-N and C-S as well).
4. It is reasonable to assume that only groups attached at one place to a large polymer or oligomer are produced as tars. Crosslinking will probably stop the group being broken off.
5. All conclusions relate to these peripheral groups described in (4). No conclusions can be made about the involatile cross-linked material.

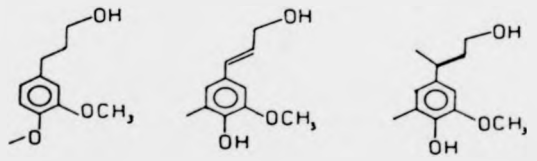
2.8 A DESCRIPTION OF COALIFICATION

The coal tars investigated fall neatly into two groups which I shall treat separately.

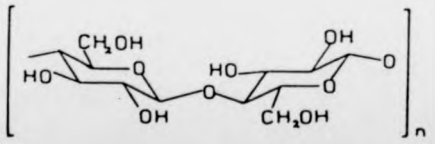
STAGE 1: WOOD TO TURKISH COAL

The two major components of wood are cellulose and lignin. These are both oxygen rich polymers made up of the following subunits:[38]

LIGNIN



CELLULOSE



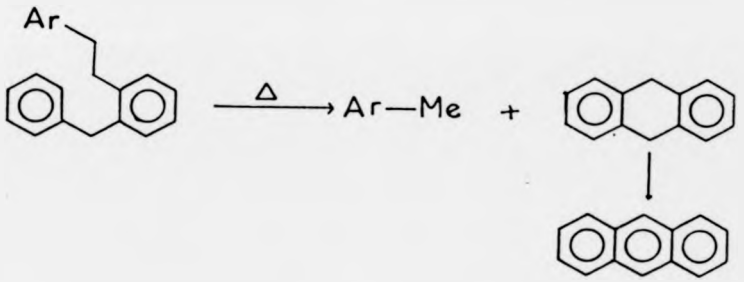
The tar produced by the pyrolysis of wood under reducing conditions has been shown earlier to be made up of acids, alcohols and a preponderance of phenols with electron-withdrawing substituents. These acidic phenols are mostly methoxy-phenols and dihydroxy-phenols. This is as one would expect from the structure of lignin indicated above. The first stage in the coalification process is biological, turning wood and other vegetation into peat. Following this the action of water, heat and pressure are responsible for coal formation. The changes in coal tar observed for these materials are:

1. A sharp decrease in tar yields.
2. A simplification of phenolics, with a loss of electron-withdrawing substituents.
3. A loss in alcohols and acids.

The decrease in tar yields is caused principally by the formation of cross-links between polymers. Cellulose and lignin are largely linear polymers and so give a large tar yield as there are always at least two peripheral groups on the polymer at all stages of pyrolysis; this is not the case for cross-linked polymers. The loss of electron-withdrawing substituents may be associated with this process. As these groups are lost, a fraction of them may be replaced by a carbon atom to form a cross-link rather than by a hydrogen atom. The loss of these groups makes a large contribution to the total loss of oxygen across these coals and coal precursors.

The discontinuity in properties between the Turkish coal and Bagworth coal is interesting. We have already seen that the tar yield and its composition changes markedly. In view of the discussion of tar yields above can we arrive at a subsidiary hypothesis to explain these observations? The oxygen content of Bagworth is less than that of the Turkish

or Australian coals and so is not responsible for the sudden increase in tar yields. Therefore the large increase in yield must be due to the breakage of some polymer links in the coal structure, increasing the number of peripheral groups available for producing tar. At about this point in coalification one begins to detect more polyaromatic materials and this could cause the cleavage of cross-links, e.g.



STAGE 2: BITUMINOUS COALS BAGWORTH - TILMANSTONE

For bituminous coals one finds only a trace of carboxylic acids and essentially no alcohols in their tars. In addition to the decrease in tar yield already discussed the following features change as a proportion of the tar.

i) The phenols increase, as does the extent to which they are alkylated. The alkylation, however decreases after the Cortonwood tar.

ii) The napthols decrease.

iii) Polyaromatic phenols become more intense in the ^{29}Si derivative spectra.

Table 4

VOLATILE O FUNCTIONALITIES AS % OF WHOLE COAL. % ad x TAR YIELD

	acids	high Ph	napthol	phenol	alcohol
Tilmanstone	trace	0.34	0.49	1.49	
Oakdale	0.05	0.16	0.47	2.06	
Cortonwood		0.77	2.51	6.36	
Linby	0.09	0.31	1.60	3.92	trace
Illinois 6	0.50	1.34	5.37	9.57	
Bagworth	0.20	0.50	3.76	5.56	trace
Turkish	0.19	0.08	0.42	2.96	0.11
Australian	0.32	0.36	1.39	1.39	0.11
Peat	3.87	1.44	2.88	5.60	0.43
Wood	4.37	9.06	7.18	4.68	5.93

It is important to note that these "increases" are part of a tar yield that decreases quite sharply across the bituminous coals (see table 3). None of the functionalities actually increases as a proportion of the whole coal, so it would be more accurate to say that the napthols are being "fixed" onto the macromolecular structure faster than the phenols. There are more points around a napthol where this could occur than on a phenol and in time this would concentrate the phenols in the tar producing material.

This process would be expected to eliminate polyaromatic phenols altogether. This is not observed; these phenols are relatively constant as a proportion of the tars. This is probably because in the latter stages of coalification condensation to polyaromatic species is occurring. The increase in methylation may be explained as a reflection of the relative rates of cross-linking with methylated and non-methylated phenols, the methyl groups inhibiting the polymerization processes.

2 9 CONCLUSIONS

The derivatization technique has been shown to differentiate between many closely related compounds, so describing the distribution of hydroxyl groups in coal tars and extracts The predictability of the chemical shifts is a particularly useful feature of the method as it means that separate regions of the silicon spectrum can be assigned uniquely to the presence of particular functional groups Using this method we have determined the distribution of hydroxyl groups between various sites in a rank series of coals and coal precursors, and of various fractions of a supercritical solvent extract (CR18). These data are presented below.

% DISTRIBUTION OF HYDROXYL GROUPS IN COAL TARS AND EXTRACTS

SAMPLE	ACIDS	'HIGHER PHENOLS'	NAPHTHOLS	PHENOLS	ALCOHOLS
TARS					
Tilmanstone	2	15	21	62	0
Oakdale	2	6	17	75	0
Cortonwood	0	8	26	66	0
Linby	1.5	5	26	63 5	0
Illinois	3	8	32	57	0
Bagworth	2	5	37.5	55 5	0
Turkish	5	2	11	78	3
Australian LY-1276	9	10	39	39	3
Peat	27	10	20	39	3
Wood	14	29	23	15	19
CR18 EXTRACT*					
Pentane solubles	8	8	16	68	0
Asphaltenes	12	19	38	31	0
Benzene insolubles	16	27	37	20	0

Data from the integrals of ^{29}Si derivative spectra

* supercritical toluene extract of Daw Mill coal

ANALYTICAL DATA FOR COALS MENTIONED IN CHAPTER 2

ULTIMATE ANALYSIS (d.m.m.f. basis)

COAL	%C	%H	%O	%N	%S*
Tilmanstone	92.4	44.5	2 0	1.45	0.67
Oakdale	90 5	5.0	2.4	1.36	0 70
Cortonwood	87 2	5 6	3.9	1.70	0 60
Linby	83.0	5.5	8.7	1 85	0.96
Illinois 6	82.5	5.5	8.8	1.46	1.70
Bagworth	80.6	5.4	11.3	1 37	0.69
Turkish	74.8	4.7	14.5	2.29	3.68
Australian LY-1276	66.9	4.9	26.3	0.74	0.36
Peat	59.5	6.0	32.3	1.95	0.24
Wood	50 8	6.2	42 7	0 13	0 02
Daw Mill	79 8	4 8	11 6	1 4	1.5

* organic sulphur
% d m m f

PROXIMATE ANALYSIS

COAL	MOISTURE %(a.d.)	ASH %(a.d.)	FIXED CARBON %(a.d.)	VOLATILE MATTER %(d.a.f.)	TAR %(d.b)
Tilmanstone	0 7	5 4	77 9	17 0	2 41
Oakdale	0.6	2.9	71.8	21 5	2.78
Cortonwood	1.0	2.2	62.1	35.8	9.98
Linby	9.8	6.2	52.2	37.9	7.08
Illinois 6	9.7	14.1	41.2	45.9	18.46
Bagworth	13.7	7.6	44.6	43.3	11.55
Turkish	16.4	22.5	25.8	57.8	5 06
Australian LY-1276	28.7	0.9	34 9	50 4	7.76
Peat	8.8	5.0	25.7	70.2	18.13
Wood	9.5	1.5	14.0	83.4	38.73
Daw Mill	6.6	13.7		39.5	

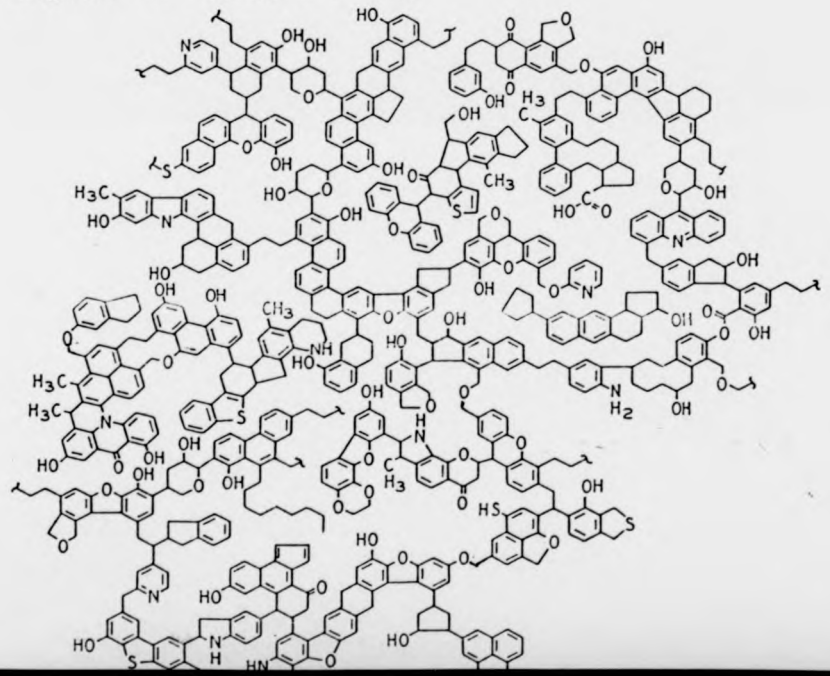
MACERAL ANALYSIS BY VOLUME (%)

COAL	CRC RANK	VITRINITE	EXINITE	INERTITE
Tilmanstone	204	65	0	35
Oakdale	301a	63	2	35
Cortonwood	501	60	12	28
Linby	802	74	10	16
Bagworth	902	72	5	23
Bersham*	502	80	5	15
Daw Mill*	802	76	9	15

* Typical values only
Petrographic data for Illinois , Turkish , Australian coals not available

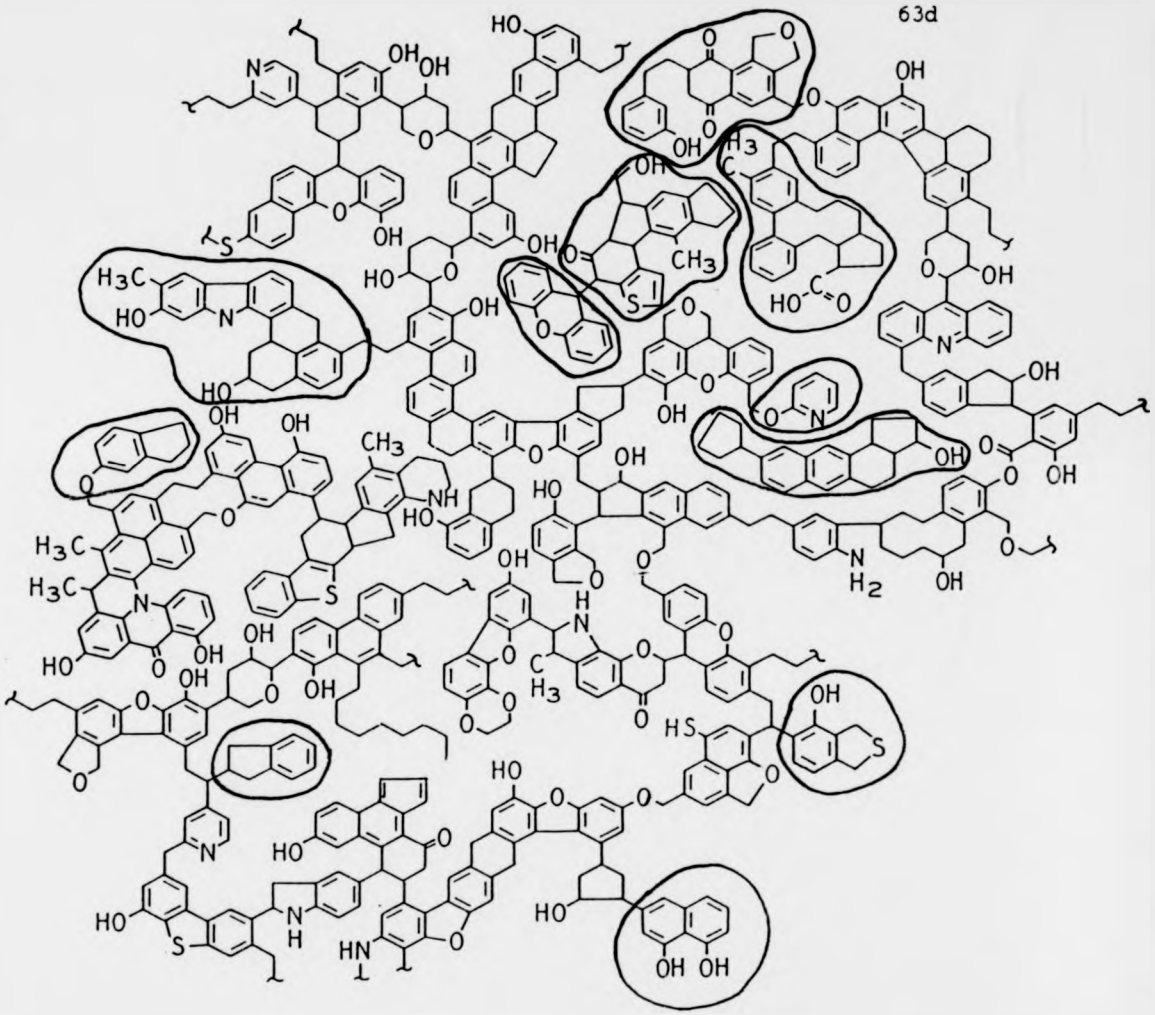
It now remains to show how these results can be used to elucidate the chemical environments of oxygen atoms in coal. Clearly this method cannot show the presence of ethers, esters, or carbonyl groups and so we must restrict ourselves to the hydroxyl environment. Aromatic ethers and esters are known to cleave during the pyrolysis of coals, forming hydroxyl species. This process complicates the description of hydroxyl groups in the original coal sample.

In order to describe the chemical environments of the hydroxyl groups it is useful to work with a coal model and try to distribute the hydroxyl groups over it according to our new data. The model we will use is that of J.H.Shinn[71] which represents a fragment of Illinois 6 coal.



This is a good modern coal model in the sense that it can be used to rationalize the behaviour of the coal under various liquefaction conditions The 600°C tar from Illinois 6 was part of the present study, and so we may use some of our results directly to improve the model

The first problem we encounter is to identify the changes to the oxygen environments that occur during tar formation The Shinn model is based on data produced from the analysis of liquefaction products During liquefaction coal is heated with a protic solvent Under such conditions ether cleavage and deoxygenation of alcohols occur The reactions that occur during pyrolysis are different as there is less hydrogen available We therefore have no reason to suspect that alcohols deoxygenate during 600°C pyrolysis as this reaction consumes much hydrogen. As discussed earlier tar formation is the result of the breaking of cross-links during pyrolysis. The fragments that are evolved as tars are those that were peripheral to the coal 'polymer'. The links that break are principally carbon-oxygen bonds, and methylene bridges between aromatic groups. The products observed are those that are volatile and as such have a low molecular weight. The effects of such a process on the Shinn model of coal structure are shown overleaf.



The 'ringed' portions of the diagram are those that might be expected to appear in coal tars, and it is the hydroxyl environment in these parts that is being observed by the ^{29}Si derivatization method.

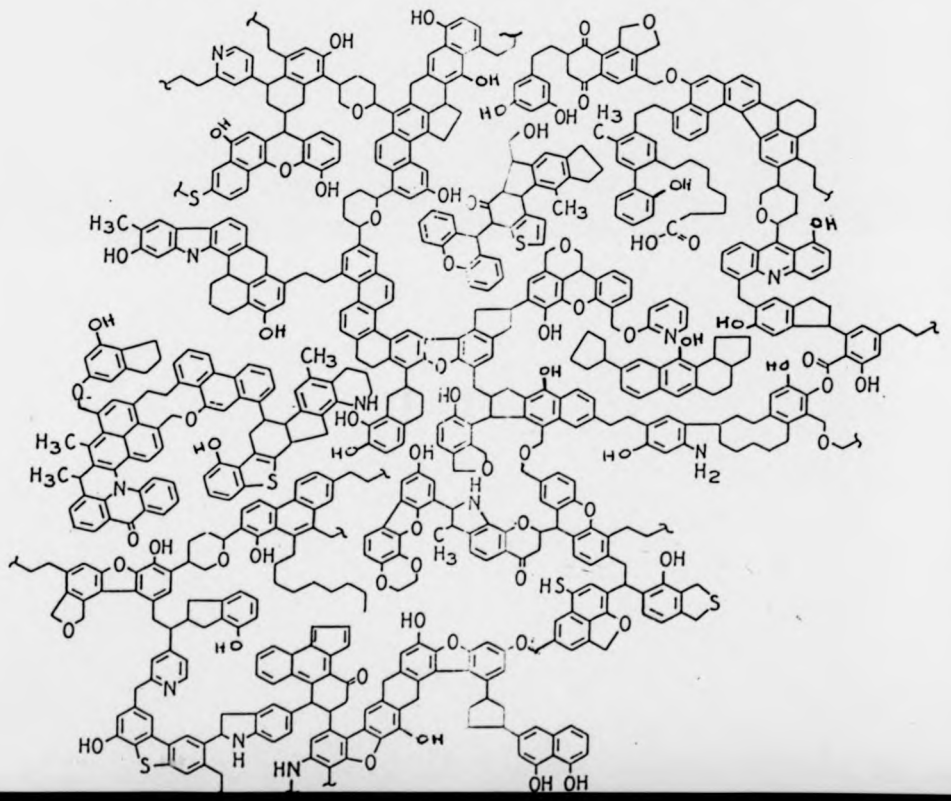
What improvements can be made to the model from our observations?

1) It is clear that the model is not large enough to show the relative proportions of acids, phenols, etc <u>for the fraction evolved as tar.</u> but if we assume that the peripheral

groups evoved as tar are representative of the whole coal, (only less cross-linked) then we may use the data to distribute the hydroxyl groups according to the results of our experiments, as shown below.

ACIDS	3%	
'HIGHER PHENOLS'	8%	Illinois 6
NAPHTHOLS	32%	600°C tar
PHENOLS	57%	
ALCOHOLS	0%	

SHINNS' MODEL OF ILLINOIS 6 WITH HYDROXYLS DISTRIBUTED ACCORDING TO THE 29SI DATA ABOVE



2) The main difference between our results and the original model are the lack of alcohols found in coal tars. These are probably not lost as water as there is less hydrogen available than in liquefaction. It therefore seems likely that hydroxyl groups in coal are almost entirely in the form of phenols.

3) Illinois 6 shows the presence of fatty acids in its tar which are not present in the original coal model

The Shinn model seems to explain our observations well in terms of the size distribution of aromatics. However the distribution of hydroxyls is markedly different from that found in our study.

As we have already seen several of the processes that occur during coalification are observable via the changes they produce in coal tars. Again these changes only inform us about the peripheral groups within a coal 'molecule'. In general as coal rank increases, the environment of oxygen atoms in coal becomes more aromatic in nature For example, peat and low rank coals show the presence of alcohols in their tars, wheras mid-rank coals are dominated by phenolics which become progressively more condensed as one moves towards anthracites.

During coalification the composition of the tar is affected by two processes.

i) Structural changes within the peripheral groups, described above.

ii) Relative rates of consolidation into the coal matrix of peripheral groups by the formation of cross-links.

Two examples of the second process have been observed.

(a) The proportion and complexity of methyl phenols increases between Turkish and Cortonwood tars, probably due to inhibited cross-linking about the hydroxyl groups.

(b) 2-Naphthols become the predominant napthol species in high rank tars. This may be explained by preferencial reaction of 1-naphthols to form cross-links due to their higher acidity. Such cross-linking will prevent them being evolved as tars on heating.

2.10 SILYLATION OF COAL PRODUCTS

Hexamethyldisilazane (200 μL, 0.95 mmole) was added to a solution of the coal tar or extract (300 mg) in deuterochloroform ($2cm^3$) containing one drop of both trimethylsilylchloride and tetramethylsilane. This mixture was shaken vigorously then left to react at room temperature in an airtight vial for four hours. After this time a white precipitate of ammonium chloride is observed. This was not removed as it did not prove detrimental to the spectra.

2.11 SILYLATION OF STANDARD COMPOUNDS

Hexamethyldisilazane (30 μL , 0.14 mmole) was added to a solution of the standard (50 mg) in deutero. Chloroform ($2cm^3$) containing one drop of both trimethylsilylchloride and tetramethylsilane. A reaction time of four hours was required for some compounds.

2.12 ACQUISITION OF SILICON SPECTRA

Silicon spectra were recorded at 74.495 MH_Z using a Bruker WH400 spectrometer equipped with a 10 mm 'VSP'probe. In order to get the required sensitivity the D.E.P.T.[39] (Distortionless Enhancement by Polarization Transfer) pulse sequence was used with broad band proton decoupling

DEPT

^1H D1 - 90° - ½J - 180° - ½J - PO - ½J - B.B.

^{29}Si 90° 180° F.I.D.

D1 = 8 seconds delay

D2 - ½J = 0.0746 second delay (J = 6.7 Hz)

Optimization of the 90° and 180° pulses together with PO are given in sections 2.13 to 2.17 .

Because of the large variety of derivatives produced when silylating coal tars and extracts many transients were required to give a good signal to noise ratio. Typically the spectra were recorded overnight giving time for about 5000 transients to be recorded.

The standard compounds that were silylated required only 32 transients in order to measure their chemical shifts. After accumulation was complete the signal to noise was improved, at the expense of 3Hz additional linewidth, by the application of an exponential window function.

Two other pulse sequences were assessed as possible methods of acquiring silicon spectra these were:

INVERSE GATED DECOUPLING

^{1}H D1 - B.B.

^{29}Si 90° FID

D1: relaxation delay of 10 seconds

This very basic sequence is employed to avoid the negative nuclear Overhauser effect (n.O.e) experienced with proton decoupled silicon spectra.[4,5] However since the relaxation time T_1 for ^{29}Si in trimethylsilyl groups is about 30 seconds it is not very sensitive. This problem can be eased by adding Cr $(acac)_3$ to the solution to decrease the relaxation time, but the improvement is not enough to compete with

the sensitivity of DEPT or INEPT which is due to the transfer of magnetization from the 9 coupled protons in the trimethylsilyl group.

I.N.E.P.T. (Insensitive Nuclei Enhanced by Polarization Transfer)

^{1}H D1 - 90° - D2 - 180° - D2 - 90° - D3 - 180° - D3 - BB

^{29}Si 180° 90° 180° FID

D1 : relaxation delay of s

D2 : ¼J for maximum polarization Transfer

D3 : a multiplicity selector $(\frac{1}{18.6J})$

The main difference between this sequence and DEPT is that if proton coupled spectra are required intensity distortions are observed of the multiplets. In our experiments this is not a problem. However INEPT only works well if the pulse angles are known accurately. Unfortunately when we started this work the "VSP" probe did not tune well to ^{29}Si and so the pulse angles were not reproducible. This caused us to use DEPT which is not as sensitive to errors in the pulses. After the probe was overhauled it tuned to silicon much more easily and INEPT then became the method of choice for observing trimethyl silyl groups.

2.13 OPTIMIZATION OF THE NMR PARAMETERS FOR DEPT AND INEPT

In order to perform polarization transfer sequences one must know the pulse angles used with some accuracy; this is especially true with the longer sequences such as INEPT .

2.14 CALIBRATING THE 90° ^{1}H PULSE

The following measurements were performed on $2cm^3$ of a 1% solution of trimethyl-silyl chloride in deuterochloroform in a 10 mm NMR tube. A normal proton spectrum of this sample was recorded from a single pulse using the decoupler coils of the 'VSP' multinuclear probe. This spectrum was recorded using a pulse width of 5 μs with the methyl resonances exactly on the proton pulse frequency. From this spectrum a standard phase correction was obtained. The pulse width was then successively increased in order to find a signal null when it reached 180°. An exact null was not found but the signal became 90° out of phase before inverting and that point corresponds to a 180° pulse. This occurred with a 60 μs pulse i.e. the ^{1}H 90° pulse on theVSP probe is 30 μs .

2.15 CALIBRATING THE ^{29}SILICON 90°PULSE

The silicon pulse length was calibrated using a sample of 85% hexamethyldisiloxane in d_6 benzene. A reasonable proton coupled ^{29}Si spectrum of this was recorded after a single pulse without using any special pulse sequences. With the pulse frequency centred on the silicon resonance the pulse length was varied in order to find a null signal. The null is not very well defined with silicon since it is an insensitive nucleus so one must interpolate from spectra recorded either side of the 180° pulse. Using this procedure the 180° pulse was found to be 40 μs , the 90° pulse 20 μs .

2.16 OPTIMIZATION OF THE MULTIPLICITY SELECTION PULSE PO

As an example of what this pulse does the effects on carbon spectra are given below.

PO = 45° CH, CH_2, CH_3 resonance all positive

PO = 90° only CH resonances observed

PO = 135° CH are positive CH_3 negative.

The problem then was to find a pulse length such that $Si(CH_3)_3$ was positive. With 9 protons all coupling equally it was not clear what the correct pulse angle should be. In order to determine this a number of DEPT spectra were recorded of a solution of trimethylsilyl-chloride in deuterochloroform with various values of PO between 1 and 20 μs .By trial and error the optimum value was found to be 7.1 μs or a 21.3° pulse.

2.17 OPTIMIZATION OF THE MULTIPLICITY SELECTION PULSE 'D3' IN THE I.N.E.P.T. EXPERIMENT

This delay was optimized by trial and error in the same way PO was (see above). A series of spectra were recorded of a dilute solution of trimethylsilyl chloride in deuterochloroform using different delays. The optimum delay for the trimethylsilyl group was found to be 8 ms or 1/18.6J.

2.18 SENSITIVITY. DEPT VS. INEPT

The solution used to optimize D3 in the INEPT experiment was also used to test the relative sensitivity of the two methods.

Spectra were recorded using the optimized parameters for both experiments with 32 transients each. The signal to noise (peak to peak) ratios for the two experiments were:

DEPT	9
INEPT	31.75

2.19 SENSITIVITY OF ^{29}SI N.M.R. USING DEPT

A solution of phenol in deuterochloroform (2mg/cm^3) was derivalized with hexamethyldisilazane (50 μl, 0.29 mmole) and trimethylsilylchloride (1 drop). A ^{29}Si spectrum of this sample was acquired using 32 transients. The signal to noise (peak to peak) ratio of the resonance was 2:1.

An overnight accumulation typically has 5000 transient giving an increase in signal to noise of

$$\sqrt{\left(\frac{5000}{32}\right)} \quad \text{or x } 12.5$$

i.e. with 5000 transients 2mg/12.5 = 0.16mg of phenol could be detected. This corresponds to a sensitivity limit of 1.7 μmole.

With the improved parameters for INEPT this is reduced to 0.5 μ mole.

RELATIVE YIELDS OF SILYLATION REACTIONS

The use of derivalization methods to analyse a complex mixture relies on the following conditions:

1. The components of the mixture must have reacted equally before accumulating data.
2. The spectral technique must give a flat response across a range of components.

These conditions were checked by derivatising two samples each containing equimolar amounts of four different components, and recording the ^{29}Si NMR spectra after 4 hours and 3 days. The composition and intensity of the components are given in table (5).

The signal intensity of each component was measured by the height of its integral in the ^{29}Si spectrum. From the figures in table (5) one can see that the technique is biased towards those components of greater acidity. Alcohols in particular only give resonances 60% as intense as those of acids.

Table 5

mixture 1	amount used m moles	intensity mm of integral	intensity / m moles	Relative Yields
benzoic acid	0.099	163	1646	100
phenol	0.091	133	1461	89
1-napthol	0.101	145	1436	87
acetic acid	0.123	161	1309	80
mixture 2				
phenol	0.111	94.5 (77)	859 (694)	89 (89)
2-phenyl-ethanol	0.093	53 (62)	570 (667)	59 (86)
ethanol	0.085	48 (41)	565 (482)	58 (62)
isopropanol	0.111	59 (60)	532 (541)	55 (69)

data taken from spectra recorded 4 hours after the derivatization.

Figures in brackets represent intensities of NMR signal after three days.

The spectra recorded after 3 days showed that the reaction of phenols and acids were complete after 4 hours whereas about 10% further reaction occurred with the alcohols after this time. However it was felt that accumulation should begin after 4 hours of reaction because the derivatives are moisture sensitive and tend to hydrolyse if left for several days. It is clear therefore that the comparison of intensities between acids and phenols and between components within a functional group is justified. Comparisons between the intensities of alcohols and those of phenols must be made only with care.

2.21 INTEGRATION OF ^{29}Si DERIVALIZED TAR/EXTRACT SPECTRA

In order to separate the hydroxyl content of a tar into separate functionalities the integrals over the following regions were measured.

> 22.5 ppm	carboxylic acids
20.75 - 22.5 ppm	"higher phenols"
19.5 - 20.75 ppm	napthols
17.5 - 19.5 ppm	phenols
16.5 - 17.5 ppm	primary alcohols

These regions are based on the chemical shifts found for standard compounds. The separation of the phenolics into the 3 classes is based on all the substituents being methyl or alkyl chains. The integrals over these regions are assumed to be proportional to the amount of derivalized materials present.

2.22 PREPARATION OF 600°C TAR SAMPLES

These samples were prepared at CRE using their equipment for performing Gray-King assays[41] (see Diagram 10). This is a device for heating coals under essentially oxygen-free conditions, the oxygen in the system being quickly replaced by coal gases. These gases are kept at atmospheric pressure throughout tar production.

The coal samples (~ 20g) were placed in the sample tube and heated immediately to 300°C then to 600°C over a period of 1 hour. They are left at 600°C for a further hour, during which time water and coal tar condense in the cooled flask. The mass of water and tar were recorded. The tar was removed from the tube and flask with dichloromethane. In order to separate the tar from the water it was washed with 50 cm^3 distilled water acidified with HCl. The tar in

dichloramethane was then evaporated to constant weight. After weighing the percentage moisture and tar of the coal were calculated. (see table 6).

Apparatus for Grey-King coke assays

Figure 10

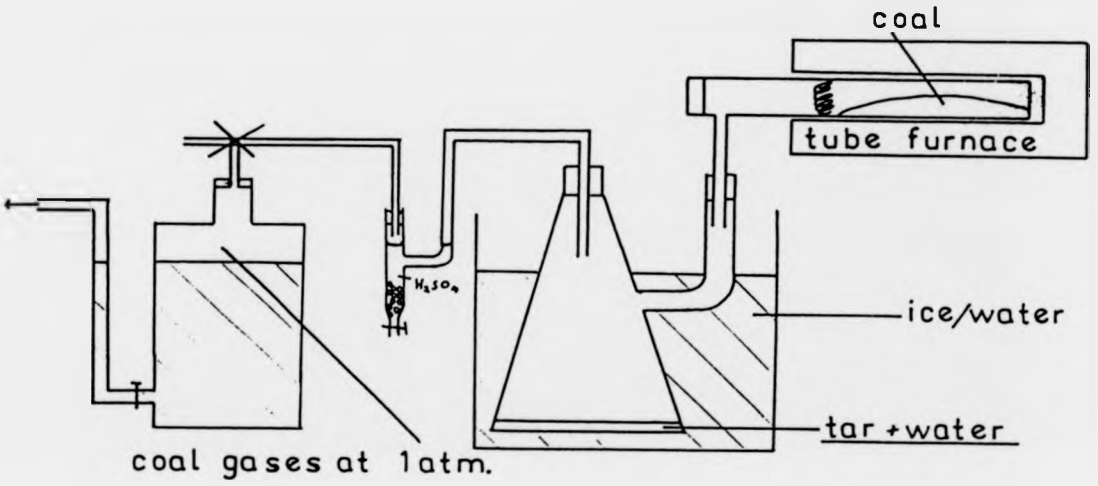


Table 6

RESULTS OF 600°C TAR PRODUCTION

material	mass used (g)	tar yield (g)	% tar d.b.	% moisture a.d.
Tilmanstone	20.706	0.493	2.41	1.50
Oakdale	20.157	0.552	2.78	1.20
Cortonwood	20.025	1.930	9.98	3.40
LINBY	19.076	1.178	7.08	12.83
Illinois No. 6	21.322	3.579	18.46	9.01
Bagworth	20.101	2.013	11.55	13.26
Turkish Lignite	19.865	0.752	5.06	25.21
Australian LY-1276 D	17.277	0.616	7.76	54.08
Peat	20.948	3.005	18.13	20.87
Wood	8.679	2.710	38.73	19.34

d.b. : dry basis

a.d. : as determined

2.23 PREPARATION OF SAMPLES FROM THE SUPERCRITICAL EXTRACT CR18 *

This is a toluene extract of DAW MILL coal performed at 420°C given to us by C.R.E. The extract represents ~35% of the whole coal and its structure is generally thought to be representative of it. The extract itself resembles that of a bituminous coal and must be further refined before use in structural studies.

2.24 PREPARATION OF SOLVENT EXTRACTS OF CR18 *

The extract (50g) was heated under reflux in benzene (1L) for 4 hours then cooled to room temperature. The suspension produced was filtered yielding a black residue of benzene insoluble materials. The filtrate was reduced to 200cm^3 in vacuo. Pentane (2L) was added slowly with stirring and left to stand for 30 minutes. This produced a precipitate of asphaltenes which was collected by filtration.

The filtrate (pentane solubles) was then evaporated to constant weight as were the asphaltenes and benzene insolubles.

50g of extract gave: 17.1 g pentane solubles
11.6 g asphaltenes
19.4 g benzene insolubles

EXTRACTION OF ACIDS FROM CR18 MATERIALS BY ANION EXCHANGE CHROMATOGRAPHY

The acidic components of the extracts were separated by binding them to the strongly basic anion exchange resin Amberlite IRA 904. This was converted from the chloride to the hydroxide form as follows.

Amberlite IRA 904 (100g) was suspended in an 8% solution of sodium

* See Appendix 2 p.p. 146 to 148 for detailed analysis.

hydroxide ($350cm^3$) for 15 minutes. The resin was filtered and washed well with distilled water until no trace of Cl^- was found in the filtrate (acidic N/10 $AgNO_3$(aq)). It was then washed with benzene ($300cm^3$) and n-pentane ($300cm^3$), dried in vacuo at 40^oC, and stored for later use.

The resin was slurried in THF and poured into a water-cooled chromatography column (30cm x 1cm). The sample (4g) was loaded on the column in a small amount of THF then eluted slowly ($1cm^3min^{-1}$) with further THF until the eluate became clear. The acids were then displaced from the resin with carbon dioxide saturated methanol ($100cm^3$) or 5% HCO_2 in THF ($100cm^3$) followed by THF ($200cm^3$). The resulting acidic solution was evaporated to constant weight. In some cases two columns were needed to get sufficient sample for ^{29}Si derivatization work.

EXTRACTION OF BASES FROM CR18 MATERIALS BY CATION EXCHANGE CHROMATOGRAPHY

These were separated by an analogous process to that above. The resin used was Amberlyst 15 a strongly acidic cation exchange resin. It was converted to the acid form by soaking in 10% CHl (aq) for 3 hours. It was then washed and dried as for the Amberlite resin. A cooled chromatography column was prepared as before and 4g of the residue from the acid extractions were eluted slowly with THF until the eluant became clear. They were displaced using n-propylamine (30%) in THF ($100cm^3$) followed by pure THF ($200cm^3$). The basic fraction was then evaporated to constant weight.

RESULTS

EXTRACTION OF ACIDS

	mass extract (g)	mass acids (g)	% Yield
Pentane solubles (1)	8.968	0.377	3.8%
Asphaltenes (2)	7.441	1.010	13.6%

EXTRACTION OF BASES

	mass extract (g)	mass acids (g)	% Yield
Pentane solubles	8.159	0.276	3.4%
Asphaltenes	7.441	1.924	25.9%

(1) displaced by CO_2 saturated methanol

(2) displaced by 5% formic acid in THF

2.24 SAMPLING OF COALS

The coal samples used in this section were mostly commercial grades (washed singles) that had been crushed and ground to -212μm. As such they may be inter-seam blends from the colliery. The Tilmanstone and Cortonwood were selected seam samples (Kent No.6 and silkstone respectively). The Illinois No.6 is from the premium coal sample program of the Argonne National Laboratory (U.S.A.).

3. ^{1}H.N.M.R. AS A DETECTOR FOR H.P.L.C. (LC-NMR)

RESULTS AND DISCUSSION

3.1. INTRODUCTION

The motive for the investigations we have undertaken has been to provide tools for the elucidation of coal structure and to demonstrate their use, e.g. the examination of inorganic materials in coal by solid state NMR and the determination of hydroxyl groups by chemical derivatization. An investigation of coal structure often involves going through the following stages:

1) The coal is degraded by heat or mild chemical methods.
2) the degradation products are separated into classes or individual components by chromatography.
3) These components are then detected and identified by some analytical technique.

The idea is to reconstruct the nature of the coal from its degradation products. Our aim in investigating the use of ^{1}H nmr as a detector for high performance liquid chromatography (H.P.L.C.) was to bring 2) and 3) together in one technique. This method is analogous to the well known technique of gc-ms. Unlike gc-ms however LC-NMR has the potential for identifying involatile components of a mixture and in addition providing structural details not available by mass spectrometry. Recent advances in LC-MS have occurred which allow detection of more involatile materials. However mass spectrometry does not in general give as much detailed structural information as NMR and hence LC-NMR may become an important technique.[41] The major problem with using NMR in this way is that its sensitivity will always be low and so a relatively large sample is required.

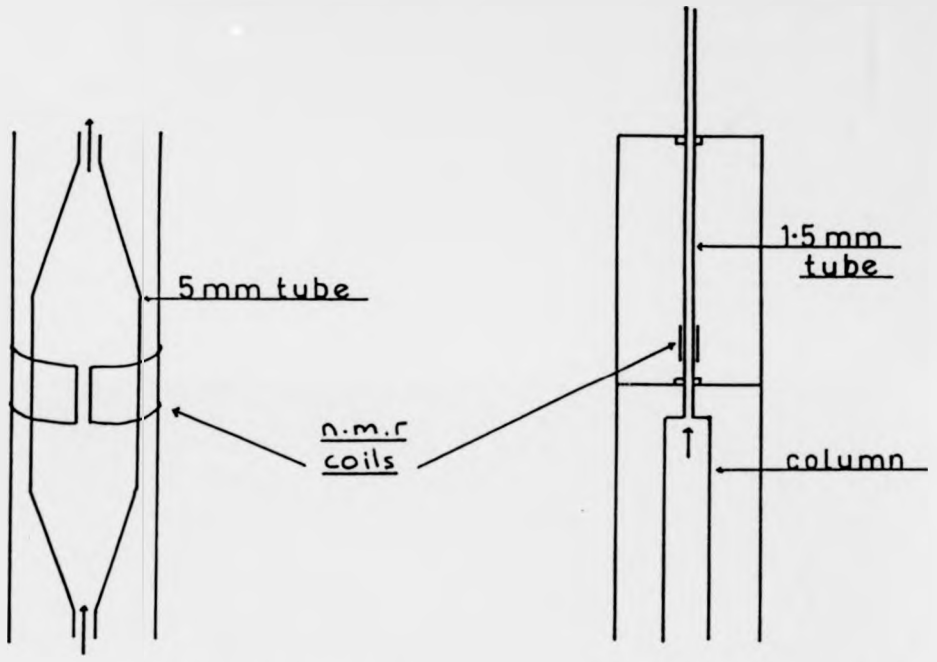
Early work in this area was done by H.C. Dorn and coworkers between 1980 and 1984.[42-46] They built a special nmr probe which contained a flow cell connected to the chromatography column. The flow cell was an integral part of the probe and so it could only be used for LC-NMR work. This option was not available to us for financial reasons so we investigated the feasibility of using a cell that could be inserted into a standard probe. This approach worked well and we achieved comparable sensitivity and resolution to previous workers.

Using this method we have examined several coal products and have shown that considerable structural data on each component may be deduced. This is the first time the technique has been used for investigating coal tar fractions. Our implementation of LC-NMR appears to have better chromatographic resolution than that of Dorn's and by presenting the data as a 2D contour plot of intensity versus chemical shift and retention time the information is much easier to interpret than for a stacked plot of individual spectra as has been used previously.

3.2 PREVIOUS WORK

The first demonstration of the use of NMR as a detector for HPLC was performed by N. Watanabe in 1978.[47] This work involved a low field NMR spectrometer and stopping the solvent flow in order to record spectra. The development of LC-NMR as a useful technique was done by Dorn at Virginia State university between 1980 and 1984 and more recently by Laude and Coworkers.[48-50] Both these groups observed the eluant whilst it was flowing through a flow cell mounted in a special probe. Diagrams and experimental parameters for these probes are given overleaf together with the sensitivity and NMR resolution of the systems.

FLOW CELLS



Dorn ref. 42 Laude ref. 48

Sensitivity	0.1 μmole ethyl benzene,	0.5 μ mole
Resolution	0.5 - 1.0 Hz ,	0.6 Hz
Cell volume	120μL ,	20μL
^1H frequency	200 MHz ,	300 MHz

After he demonstrated the feasibility of using NMR to detect fractions from HPLC Dorn used the technique to analyse a coal conversion recycle solvent. This material proved to be highly aliphatic as expected but possibly as a result of this the chromatographic separation was poor. It is more likely however that the chromatography column used was overloaded by adding neat samples in an attempt to get improved sensitivity.[44] Having produced a ^{1}H chromatogram of a coal product Dorn wished to characterize it in terms of average composition parameters e.g. % methyl aromatic, % ethyl aromatic etc. This can be done if the LC-NMR technique is done under conditions where its results are quantitative.[46] This is hard to achieve since one must have many samples to characterize each chromatographic peak accurately, which means sample times must be low with an inevitable loss in sensitivity. This is in direct conflict with the aim of improving quantification as good signal to noise is essential if NMR techniques are to be quantitative. However using LC-NMR they managed to produce an average composition analysis of a petroleum fraction.[45]

In recent years the range of samples accessible to LC-NMR has been increased by the work of Laude and coworkers.[49-50] They have shown that solvent suppression methods may be used with LC-NMR thereby allowing one to use reverse phase chromatography.[49] Again this loses some sensitivity due to the time required to saturate the solvent resonance, when the sample passes the detection coils unnoticed. The advantages of the technique are however considerable as they allow mixtures of peptides and aminoacids to be separated. Coal samples contain a huge variety of different species and any loss of sensitivity is serious, so one does not use protonated solvents.

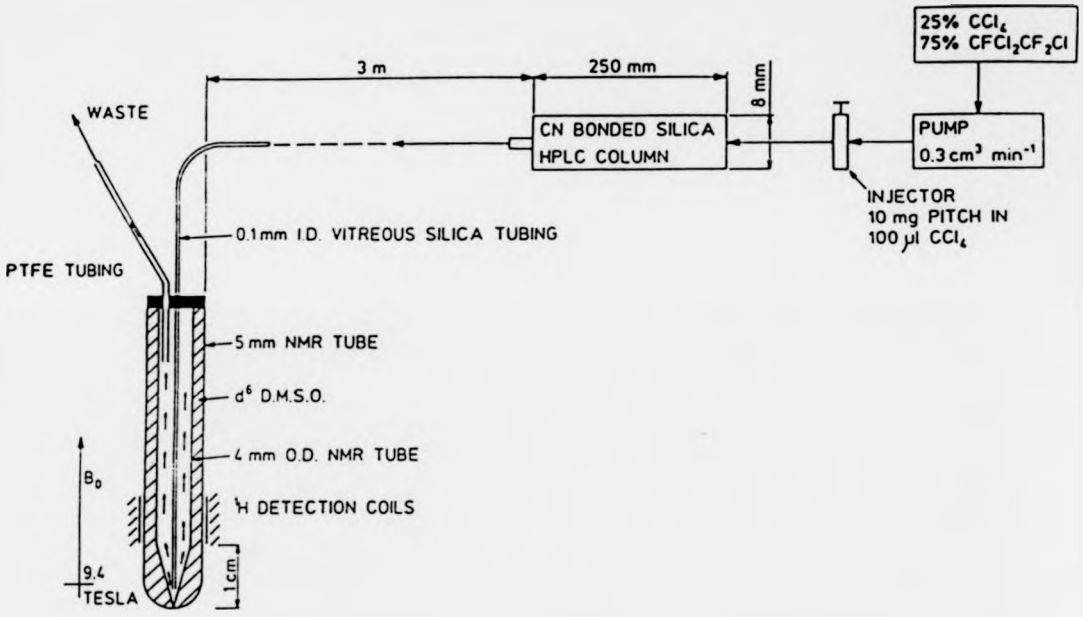
3.3 FACTORS AFFECTING THE SENSITIVITY AND RESOLUTION OF THE SYSTEM

The limiting factor for LC-NMR is always sensitivity and so the design of our system is chosen to maximise this. The important point is that a large sample is used (10 mg) so a relatively large column is needed. In order to inject a sample of 10mg a sample loop of 100μL was fitted to the chromatograph. It is obvious that there is no point having an active sample volume of less than 100μL, as with our column the chromatographic linewidth was about 0.5cm^3. This is four times that of the active sample volume (120μL) of our cell, sufficient to describe a chromatographic lineshape.

Having a large sample cell however is not sufficient for good sensitivity. The eluants must have time to become polarized by the magnetic field before they can be observed. This condition necessitates having a low solvent flow rate. With our equipment the lowest flow rate available was 0.3 cm^3 min^{-1}. This was found not to degrade the chromatographic resolution and was long enough to allow complete polarization of the sample (see section 3.15). Faster flow rates quickly reduce the efficiency of the system due to a decrease in polarization and an increase in relaxation rate and hence linewidth. Because the relaxation rates of coal materials in CCl_4 was found to be fast we were able to use a relatively fast pulse rate of about 1 pulse per second. Over a 10 ppm sweep range this reduces the digital resolution to about 1Hz, however the nature of the flow cell precludes resolution better than this even with greater digitization. The pursuit of good NMR resolution and lineshape is important since the narrower the resonances the higher the peak height. In normal NMR techniques the sample is spun to average out lateral magnetic field inhomogeneities and high

precision tubes are used so as not to disturb the vertical symmetry of the magnetic field. In LC-NMR as we have performed it, neither of these conditions can be met because the delivery tube for the cell must pass between the coils and hence disturb the magnetic field. These problems cause "shimming" to become very tricky but crucial to the final sensitivity. This is one of the two reasons our system is not as sensitive as one with a purpose-built probe. The other is that the observation coils are not mounted directly on the sample tube. This extra distance between the sample and the coils reduces their sensitivity.

3.4 GENERAL PROCEDURE



The implemenation of LC-NMR is described below in three stages. This section gives general information on the technique, the conditions quoted are typical of those used for separating and detecting poly-aromatic hydrocarbons. More detailed information is given in the section on specific experiments, and optimization of parameters and equipment.

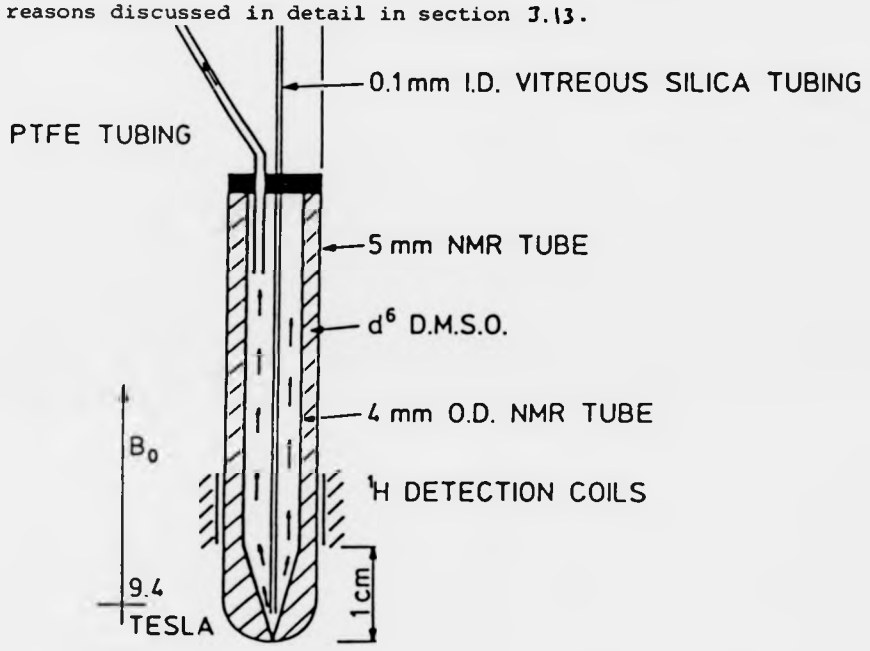
HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

A 100 µL solution of sample in CCl_4 is injected into a stream of 25% CCl_4 in $CFCl_2CF_2Cl$ provided by the high pressure pump. The sample then passes on to a nitrile bonded silica column for separation. The flow rate of the solvent is set to 0.3 $cm^3 min^{-1}$ and chromatography is complete after about 1 hour. The eluate passes from the column down 4 metres of 0.1 mm I.D. silica tubing to the flow cell. The pump is on continuously and ^1H Spectra are recorded with the solvent and fractions in motion up the flow cell.

FLOW CELL

The flow cell shown in the diagram below sits in the probehead as a normal nmr tube does. The eluant from the column comes down the silica tube and emerges at the bottom of the cell. The fractions then move up the cell and past the detection coils of the Spectrometer. The sample time used in most experiments was 1 minute and therefore the volume passing the coils was $0.3cm^3$. This is about half the volume of an average fraction. Finally as the eluant reaches the top of the cell it is removed down a waste pipe.

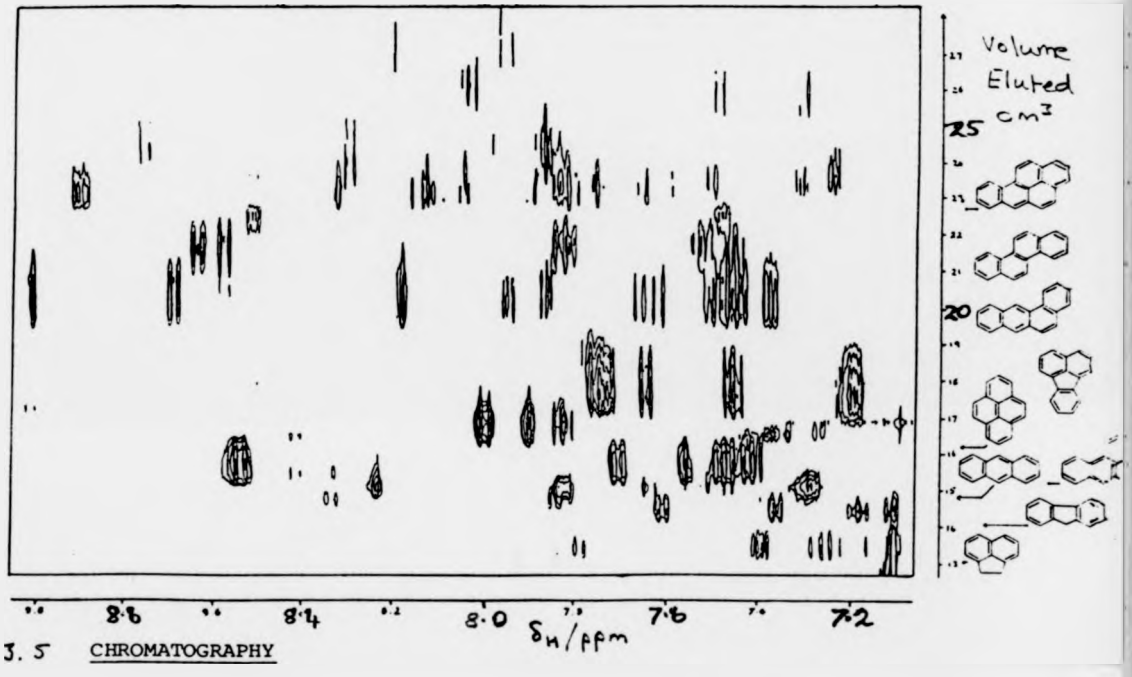
Of the designs tested the one shown below was clearly the best for reasons discussed in detail in section 3.13.



^{1}H N.M.R. detection

As mentioned above, the chromatography is continuous. There are no pauses for spectra to be accumulated. Therefore spectra must be recorded continuously. This was done using a pulse program adapted

from a kinetics experiment. This program collects F.I.D.s of 8K data points and a sweep width of 10 ppm in a continuous manner. Every 64 scans, the accumulated FID is stored as one element of a serial file, and another 64 scans are accumulated. This produces a serial file containing 64 different F.I.D. each representing $0.3cm^3$ of the eluant from the column. The 64 F.I.D. are then transformed to 64 Spectra using the 2D software available. A Gaussian multiplier and a single phase correction are applied to all 64 Spectra during transformation, the phase correction being determined from manual phasing of one of the files. These spectra are now referenced to $CHCl_3$/TMS etc and displayed as a contour plot.



3.5 CHROMATOGRAPHY

A normal phase system using non protonated solvents i.e. freons and deuterated solvents, capable of handling up to 10mg of relatively non polar materials. The chromatography is performed at a flow rate of $0.3cm^3min^{-1}$ which determines the total time required for the experiment at 1¼ hours.

NMR

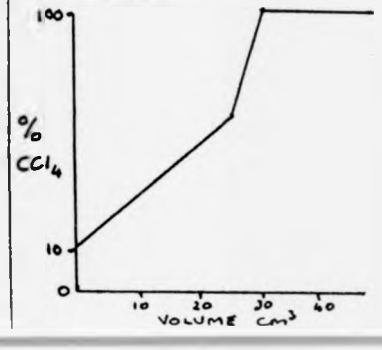
The sensitivity has been shown to be between 0.2 and 0.7 μmoles of ethyl benzene. In actual coal fraction experiments we have observed all components that were determined by other methods to make up more than 1% of the total. The resolving power of the spectroscopy is about 1Hz; sufficient to identify many polyaromatic hydrocarbons unambiguously.

3.6 RESULTS ON COAL PRODUCTS

The results shown below were produced from LC-NMR experiments performed on samples provided for us by C.R.E. They were chosen both to test the system and provide information on the materials themselves. In particular the Nantgarw tar was a very complex material and LC-NMR provided several previously undetected components. The work on the methylated Bersham tar complements the silicon derivatization work described in Chapter 2 . In order to confirm our assignments of polyaromatic hydrocarbons several 2D COSY spectra of the samples were recorded. These were highly complex spectra but provided confirmation of several structures. It is not possible to identify all the aromatics in this way however because the spin systems of many of them are very similar, causing considerable spectral overlap.

EXPERIMENTAL CONDITIONS FOR LC-NMR

Table 7

Sample	Solvent	Volume eluted before accumulation	Sample size	No. of samples	Cell used
Anthracene oil	25% CCl_4 in $CFCl_2CF_2Cl$	6 cm^3	0.35cm^3	48	5mm, no lock
Cyclohexane solubles of Avenue pitch	25% CCl_4 in $CFCl_2CF_2Cl$	8cm^3	0.35cm^3	64	4mm dmso lock
Nantgarw Aromatics	20% CCl_4 in $CFCl_2CF_2Cl$	6cm^3	0.37cm^3	64	4mm dmso lock
Methylated Bersham tar	Solvent Gradient of CCl_4 in $CFCl_2CF_2Cl$ 	6cm^3	0.45cm^3	64	5mm no lock

3.7 ANTHRACENE OIL

This coal product was chosen for our first LC-NMR experiments. It has a well-known composition of low molecular weight polyaromatic hydrocarbons as determined by gc.ms. It is therefore relatively simple to get good chromatographic resolution as the components need only to be separated by ring size; this is possible without using solvent gradients. However the sample is complex enough to show several of the important features of LC-NMR.

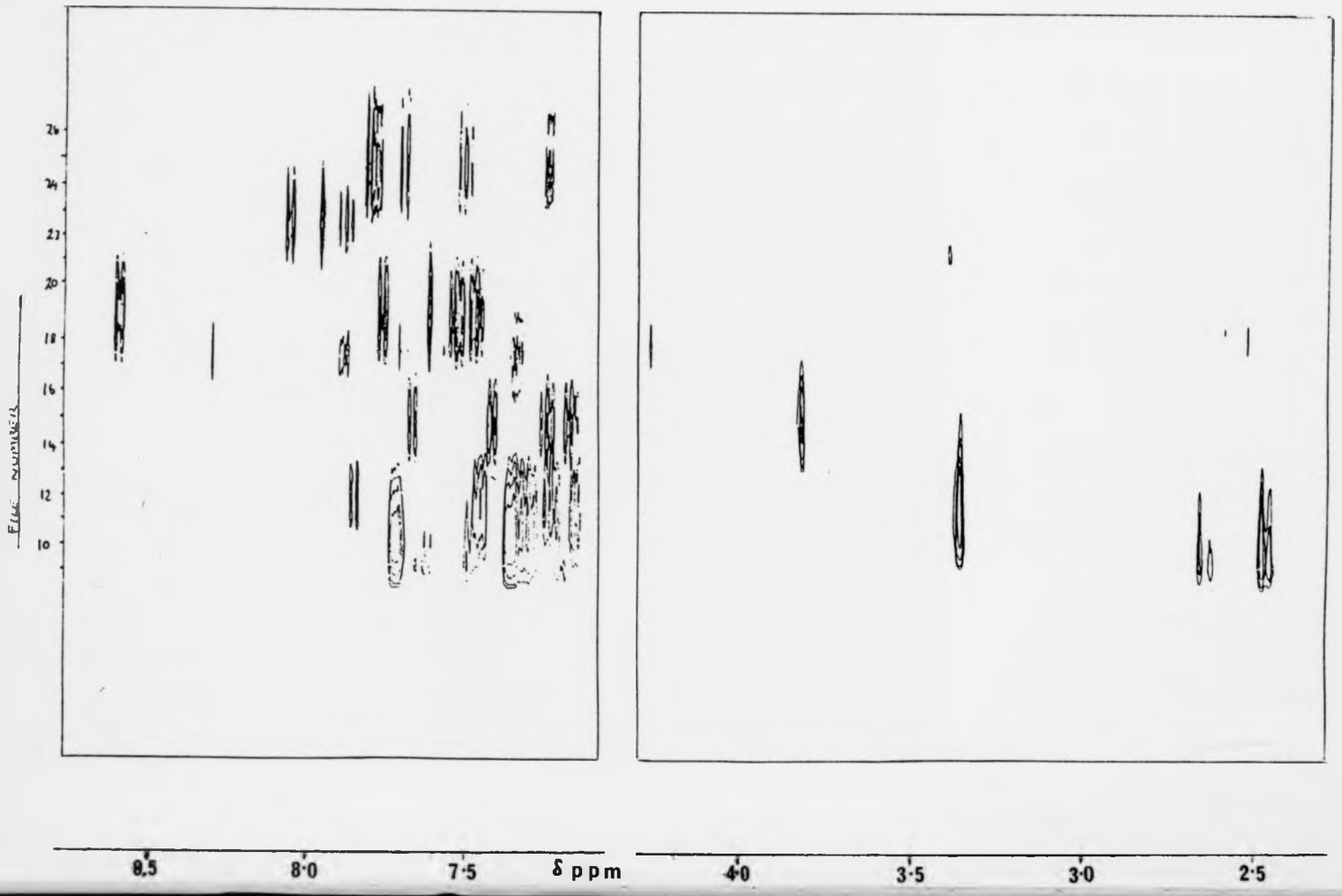
i) Structural isomers are very easy to distinguish e.g. anthracene from phenanthrene.[51]

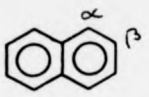
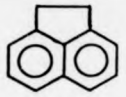
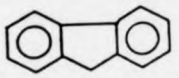
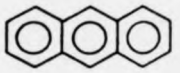
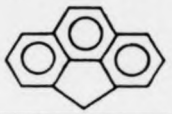
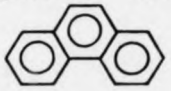
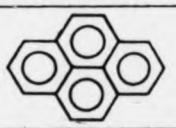
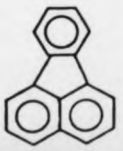
ii) Added resolution is given by having 2 dimensions in which to distinguish components. For example napthalene and fluorene are not resolved chromatographically; however they are very easy to distinguish in the 2D contour plot

iii) On the basis of the g.c. data available for this mixture the LC-NMR experiment has detected all the components greater than 1 % of the total. This is using the 5mm flow cell. The next sample was investigated using the 4mm cell and is of much higher quality.

Figure 11

Anthracene oil



File number	Chemical Shift (ppm)	Interpretation
8	7.73(m) 7.37(m) 2.65(s) 2.48(s)	 napthalene - methyl napthalenes - methyl napthalenes
9	7.16(d) 7.24(t) 7.32(d) 3.37(s)	 acenapthene aliphalic protons
14	7.68(d) 7.42(d) 7.25(t) 7.18(t) 3.83(s)	 fluorene CH_2 bridge
17	8.40(s) 7.90(m) 7.35(m)	 anthracene 8.40ppm of this type of proton. c.f. benz[a] anthracene
17	4.28(s)	a weak resonance possibly due to the aliphatic protons of 
18	8.60(d) 7.78(d) 7.60(s) 7.53(t) 7.48(t)	typical of "internal" protons i.e.  phenanthrene
21	8.05(d) 7.95(s) 7.77(t)	pyrene 
23	7.80(m),(d) 7.70(d) 7.53(t) 7.27(m)	fluoranthene 

3.8 CYCLOHEXANE SOLUBLES OF AVENUE PITCH

This sample is almost exclusively made up of polyaromatic hydrocarbons. It contains more types than the anthracene oil and was used to test the improved flow cell. The chromatogram shown overleaf contains several notable features:

i) excellent chromatographic resolution especially considering the limited choice of solvents available, which has separated the components very efficiently by size.

ii) many isomers may be identified that have the same molecular weight and very similar structure. This is difficult or impossible by gc-ms except on the basis of retention times of standard compounds.
e.g. of the four ring aromatics the following have been identified.

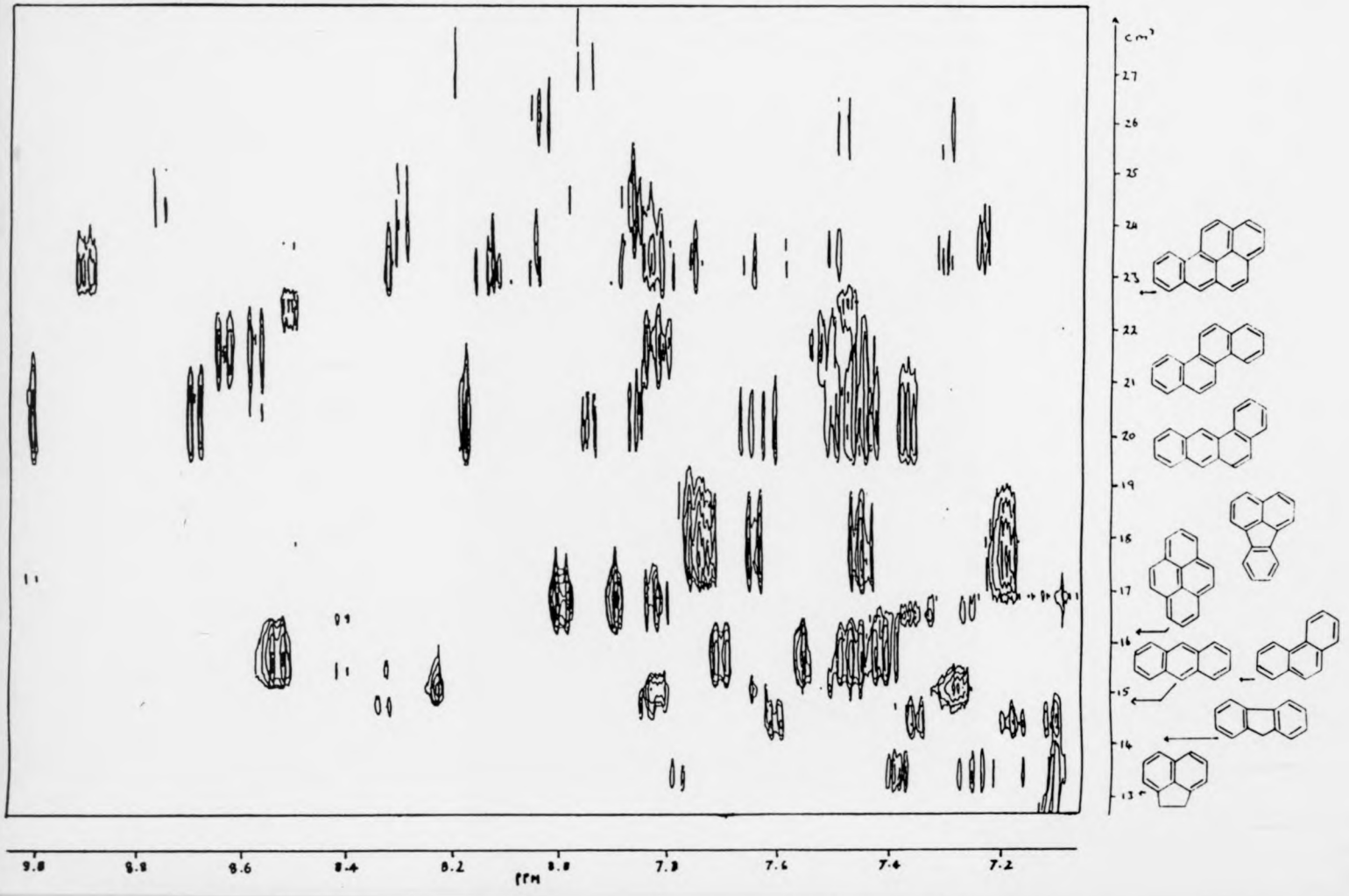
$C_{16}H_{10}$: pyrene, fluoranthene

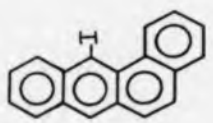
$C_{18}H_{12}$: benzanthracene, crysene, benz phenanthrene

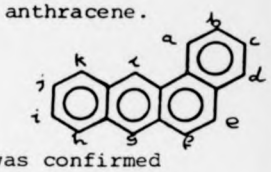
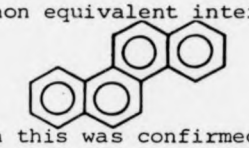
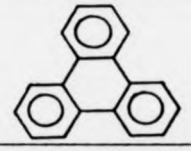
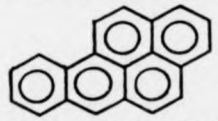
iii) sensitivity much improved over the 5mm cell.

CYCLOHEXANE SOLUBLES OF AVENUE PITCH

Figure 12



Elution Volume (cm^3)	Chemical Shift	Interpretation
13		acenapthene perhaps but several other resonances are present
14.5	7.6(d) 7.4(d) 7.2(t)	fluorene
15	7.8(m) 7.3(m) 8.3(s)	anthracene
15.5	8.55(d) 7.70(d) 7.55(s) 7.5 (t) 7.4(t)	phenanthrene
16.5	8.0(d) 7.9(s) 7.8(t)	pyrene
17.5	7.75(d)+(m) 7.65(d) 7.45(t) 7.2(m)	fluoranthene
20	9.0(s)	shift characteristic of internal proton. But it is a singlet therefore it must be 

Elution Volume	Chemical Shift	Interpretation
	8.7(d) 8.2(s) 7.4(t)	This material is benz a anthracene. proton a g (d)  The complete structure was confirmed by a COSY experiment on the whole material.
21	8.65(d) 8.60(d)	Two non equivalent internal protons  crysene Again this was confirmed by 2D nmr.
22	8.7(m) 7.5(m)	
23	9.9(d)+(d) 8.3(s)	 Evidence is sparse for this compound. However it does have 2 'internal' protons and an anthracene like proton. The retention volume is also consistent with this structure.

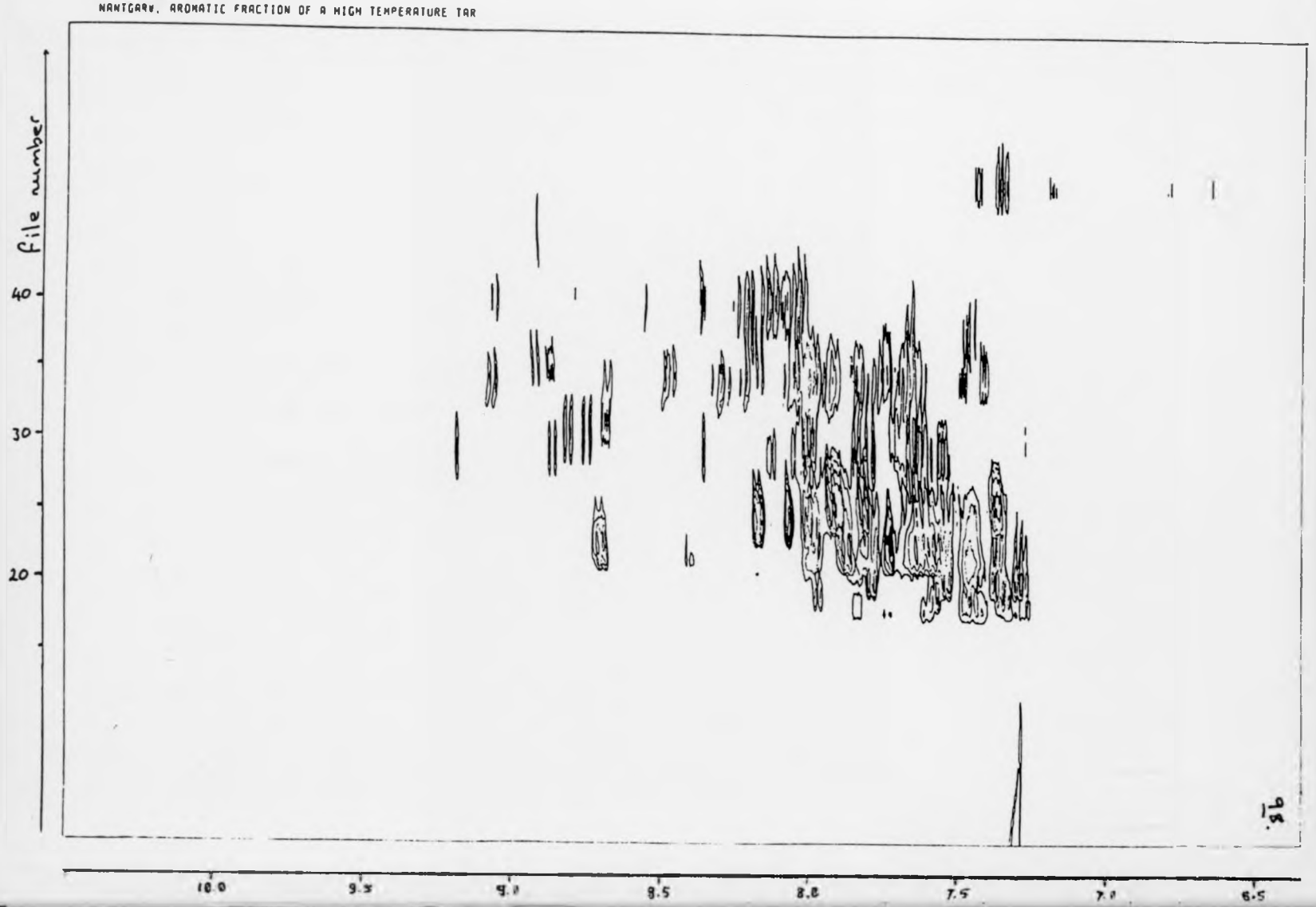
3.9 AROMATIC FRACTION OF A HIGH TEMPERATURE TAR (NANTGARW)

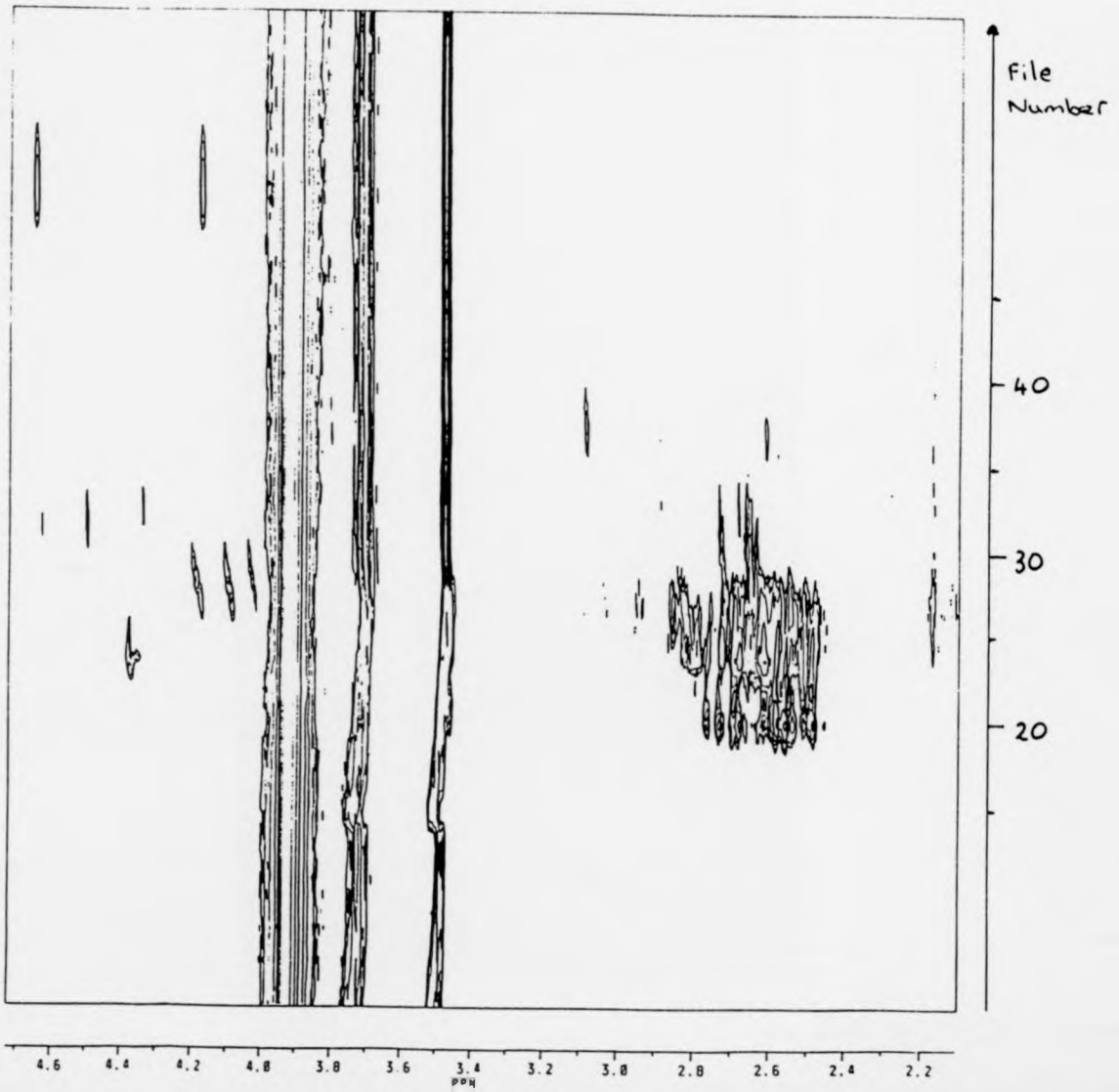
This fraction was produced at CRE by silica chromatography of a tar from a high rank bituminous coal. The aromatics are that fraction that is eluted by benzene but not by pentane. As can be seen from the NMR chromatogram this is a very complex material.

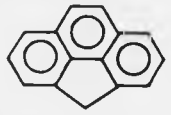
The principle difference between this sample and the Avenue pitch is the degree of alkylation. This makes this sample a particularly tough test because the number of possible isomers for a methyl aromatic hydrocarbon is very large and so the intensity of the aromatic protons is reduced as the resonances of different isomers are not coincident. The major points of interest on this chromatogram are found in the aliphatic portion of the spectra. These include many species containing methylene bridges between aromatic groups δ= 4.0 - 4.6 ppm and methyl aromatic resonances around 2.7 ppm. The most impressive features of the chromatogram are the 9 different benzfluorenes; the non methylated materials are not separated chromatographically; however they are by NMR. The reverse is true of the methylated and dimethylated analogous; in particular only a combination of NMR and HPLC can show that there are 9 distinct species present.

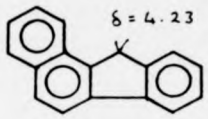
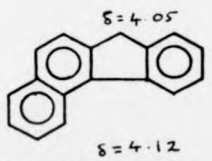
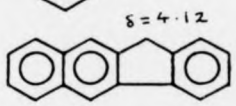
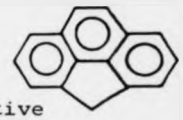
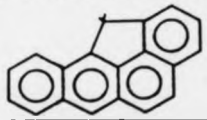
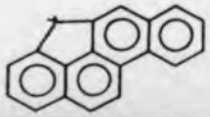
Figure 13

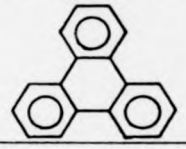
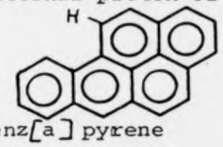
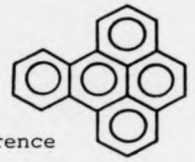
NANTGARW. AROMATIC FRACTION OF A HIGH TEMPERATURE TAR




File
Number
40
30
20
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
PPM

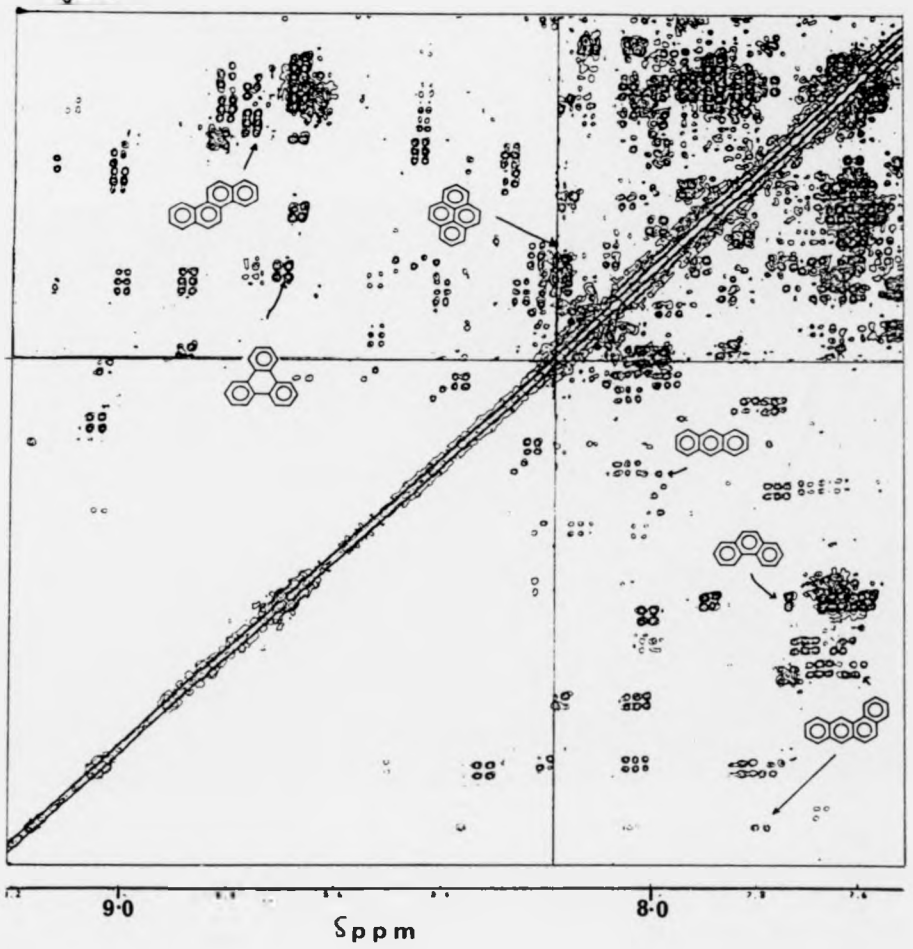
Sample No.	Chemical Shift	Interpretations
17	7.85(m) 7.45(m) 2.8-2.65(s) 2.65.2.4(s)	napthalene + many methyl napthalenes α - methyls β - methyls
18	3.48's) 7.58(d)	due to acenapthene. There is some methylation causing a blurring of the aromatics.
20	7.77(d) 7.5(d) 7.36(t) 7.28(t)	characteristic aromatics of fluorene. These are clear because there is little methylation (2.4 - 3ppm). The CH_2 of fluorene is obscured by water in the dmso lock solvent.
21	4.4(s)	 $\delta = 4.4$ ppm due to the effect of several ring currents. It elutes before pyrene. c.f. fluorene elutes before anthracene. The two small subsidiary peaks are due to methylated variants.
22		anthracene + phenanthrene These are highly methylated as shown by the aliphatic region as well as being common as the basic structures.
24	8.15(d) 8.05(s) 7.98(t) 2.85(s)	pyrene methyl pyrene
25	7.85(d)+(m) 7.65(t) 7.95 (d) 7.4(m)	fluoranthene. Unclear due to many other resonances but more obvious from the 2D COSY spectrum. Probably some methyl fluoranthenes present.

Sample No.	Chemical Shift (ppm)	Interpretation
24 - 29	4 - 4.2(s)	9 singlets in 3 groups.   benzofluorenes  Each of these gives 3 distinct peaks due to dimethylated, monomethylated and non-methylated variants. The dimethylated elute first, the non methylated last; note that there are no Me-Ar resonances in file 29. These materials elute before the benzanthracenes in the same way that fluorene elutes before anthracene.
29	9.2(s) 8.35(s) 8.85(d) 2.7(s)	benz[a]anthracene methylation of 4 ring aromatics is very sparse.
29	4.5(s)	Characteristic of  but must be a benzo derivative for example 
30	8.82(d) 8.75(d) 4.3(s)	crysene possibly 

Sample No.	Chemical Shift	Interpretations
32	8.70(m)	napthalene type peak. COSY shows this is coupled only to a resonance at 7.65 ppm and that is coupled to no other protons. 
34 - 40		Beyond this point the number of isomers of polyaromatic hydrocarbons becomes very large making a detailed assignment impossible. 5-ring aromatics
36 - 40	9.0(d)	internal proton of type  benz[a] pyrene But not
	9.9(d)+(m)	benz[e] pyrene  identified from reference
40 - 45		5-ring aromatics

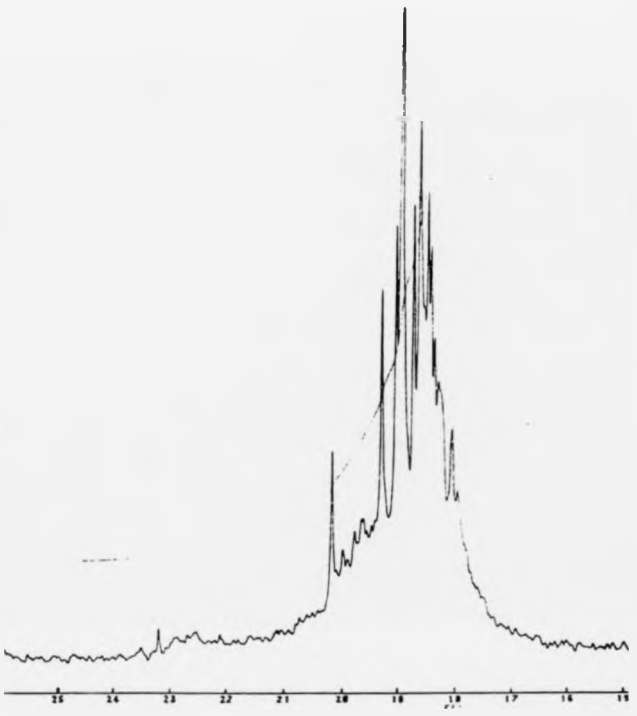
PART OF THE 'COSY' SPECTRUM OF NANTGARW AROMATICS

Figure 14



3.10 METHYLATED BERSHAM TAR *

This material is a tar similar to those produced during our ^{29}Si derivatization study. It was methylated in order to reduce its polarity and make it more amenable to chromatography. The silicon derivative spectrum of the unmethylated tar is shown below.

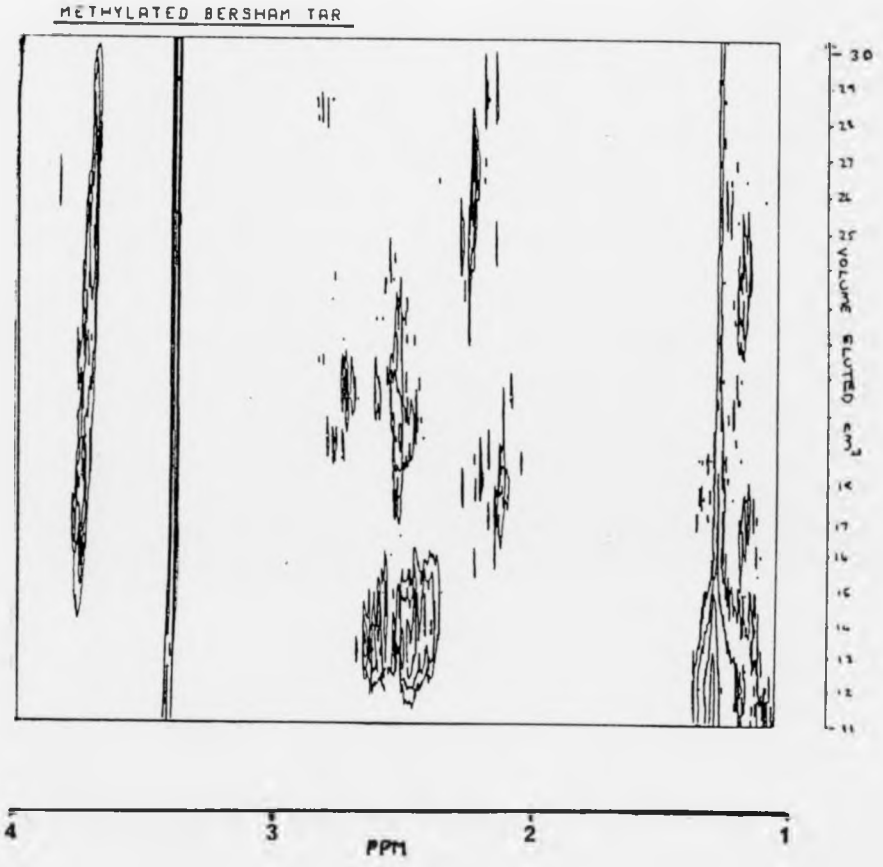


This shows that the principle components of the tar are methyl phenols and napthols. However it is impossible from the silicon spectra to infer the exact nature of the alkyl substituents on phenols or the nature of the material containing no hydroxyl groups. The chromatogram overleaf should be seen as complementary to the silicon spectrum above. In particular it shows that the sample contains much

* Details on p. 124.

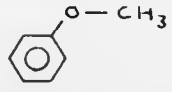
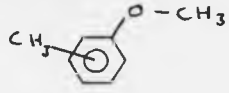
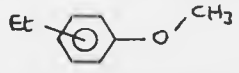
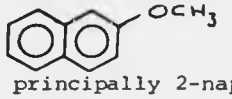
methylnapthalenes, the phenols are methyl and ethyl substituted whereas the napthols are principally methyl substituted. It also shows traces of larger aromatic material e.g. methyl anthracenes and phenanthrenes although PAH as such are not important components of this sample.

Figure 15



PAGINATION ERROR

P 106

Elution volume cm^3	Chemical Shift	Interpretation
15	1.0 - 1.4	alkanes; possibly alkyl benzenes
12 - 16	2.3 - 2.7	methyl napthalenes > 2.55 ppm are ∝ methyls.
15 - 20	3.7	 from the methylation of phenol. As the chromatography progresses methylated cresols and xylenols are eluted.
	2.2	 various
	2.5/1.2	signs of ethyl aromatics. i.e.  The alkyl phenol derivatives are no longer present after about 20 cm^3. As the heavier alkyl napthols take over.
20 - 30	3.6	 known to be principally 2-napthols from our study of silicon derivatives of coal tars.
	2.3	methyl napthols. 1 type predominates, however we cannot say which one.
21 20	8.7(a) 8.4(s)	phenanthrene anthracene
21	2.7	methyl phenanthrenes
20	2.8	methyl anthracenes

3.11 CONCLUSIONS

We have shown that LC-NMR may be implemented without the expense of building special probes and that the sensitivity achieved is sufficient to discover much about the composition of coal products. Neither the chromatographic nor NMR resolutions are compromised to an unacceptable degree. The principal advantages of the techqique are the ease of identification of fractions without recourse to retention time data for a very large number of standards, and the ease of distinguishing many closely related compounds.

EXPERIMENTAL TO CHAPTER 3

This section gives both the experimental details of our LC-NMR work together with some of the problems encountered and how they were overcome. The sections are in the order of appearance in the experiment i.e. chromatography, flow cell followed by NMR acquisition and spectra presentation.

3.12 OPTIMIZATION OF CHROMATOGRAPHIC CONDITIONS

The High Performance Liquid Chromatography (HPLC) equipment we used was lent to us from the coal research establishment (CRE). It consisted of the following:-

Applied Chromatography Systems pump, model 750/03

Rheodyne injector with 100 μL sample loop

Du Pont Spectrophotometer (837)

Hi Chrom Columns: S5CN-25004

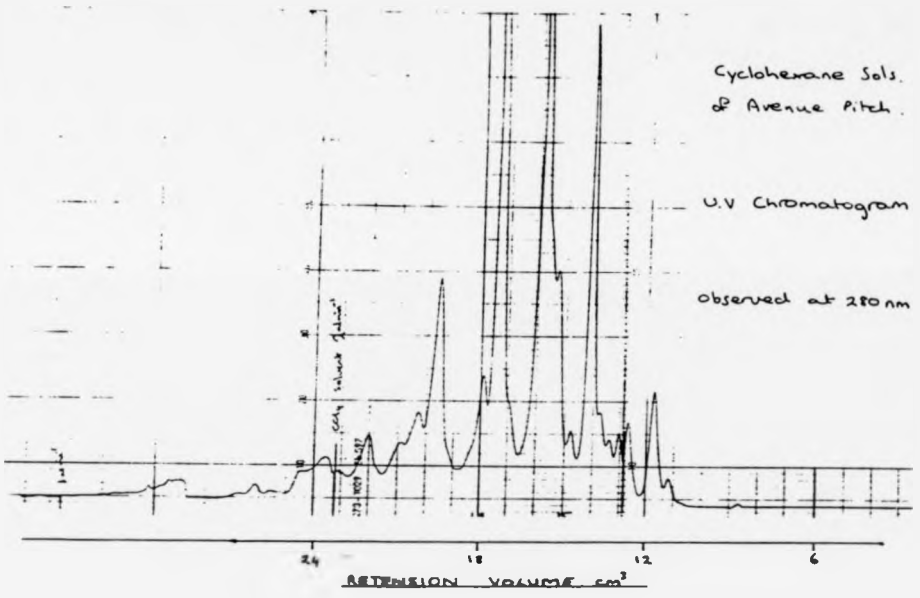
S5NH-25072

S5W-25037

The columns had previously been found suitable for medium scale HPLC of coal materials by the staff of CRE. They can all manage 10mg of sample per run and the bonded phase columns are extremely robust and give consistent results even after very heavy use.

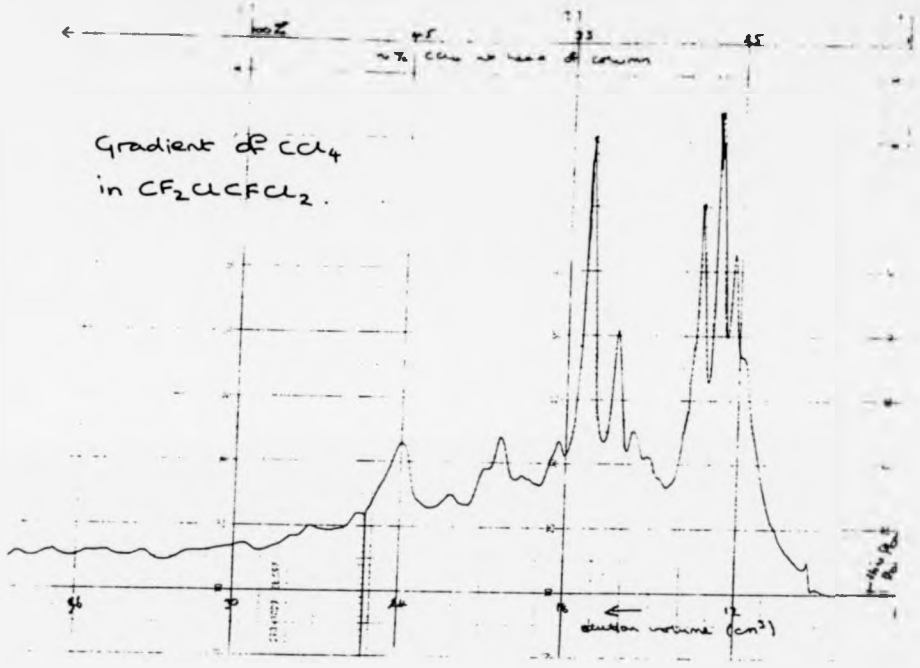
We set out to find a chromatography system that could separate 10mg of polyaromatic hydrocarbons (PAH). Our experiments were all done using analytical scale samples because otherwise one overloads the U.V. detector. Our first attempts involved using a mixture of various PAH and attempting to separate it using CCl_4 as solvent with the three columns above. In this way we found that the nitrile bonded silica column was the most suitable. However CCl_4 itself elutes PAH too quickly and poor resolution results so we had to find a solvent that would slow down this solution. The ideal choice turned out to be 1, 1, 2 trifluorotrichloroethane. This is available commercially in HPLC grade and is relatively cheap.

Using a 25% solution of CCl_4 in $CFCl_2CF_2Cl$ we achieved the following chromatogram of the cyclohexane solubles of Avenue pitch.



The chromatography was found to be just as efficient when the solvent flow rate was reduced to $0.3 cm^3 min^{-1}$ even though the optimum flow rate for this column is quoted as $2.0\ cm^3 min^{-1}$.

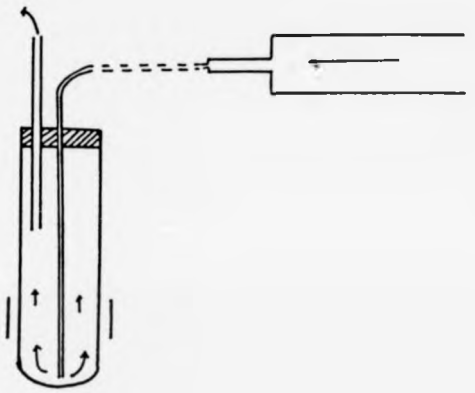
This solvent system proved effective for all the less polar samples. The methylated Bersham tar however is more tricky. It contains a wide variety of polarities and could only be separated effectively using gradient elution. In this way the following chromatogram was obtained:



In conclusion, because of the necessary absence of protons in the solvent the normal separation conditons for PAH i.e. reverse phase acetonitrile/water method may not be used. The solution is to perform the chromatography in the normal phase manner using various "freons" as solvents. This is considerably cheaper than using deuterated solvents, and gives a better NMR sensitivity than performing solvent suppression methods.

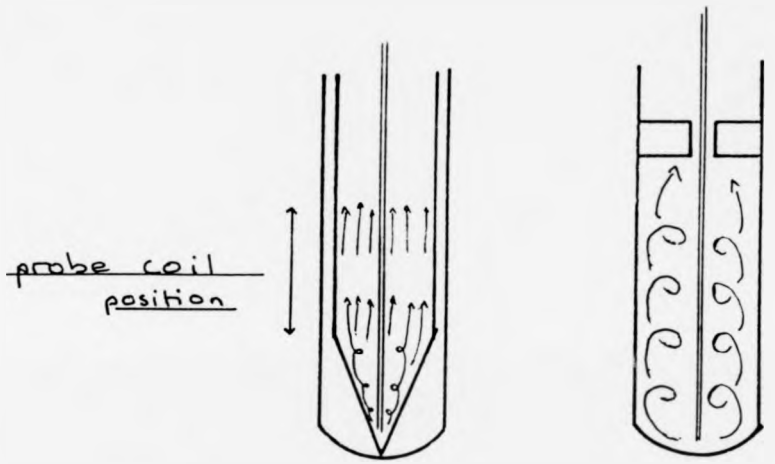
3.13 THE FLOW CELL FOR LC-NMR

The type of flow cell needed for LC-NMR is dictated by the configuration of magnet and probes available for the spectrometer. In our case this meant that the delivery and waste tubes of the cell had to emerge from the top of the magnet. This implies that the cell must be a variation on:



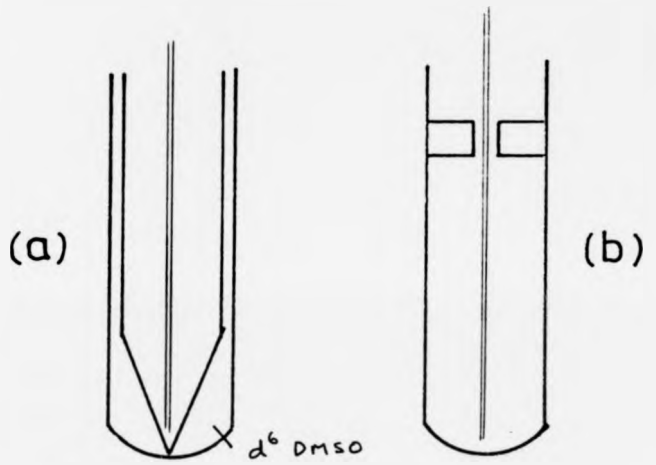
The chromatography equipment must be placed well away from the spectrometer to avoid distorting the magnetic field, and so the delivery tube must be several metres long. In order that it has a very low dead volume and that it does not interfere with the active sample volume it must be very narrow. An ideal material for such a purpose is vitreous silica tubing used for gas chromatography, this has an internal diameter of 0.1mm with an outside diameter of $\sim$ 0.5mm.

Having such a small aperture on the delivery tube does cause problems. At a flow rate of $0.3cm^3min^{-1}$ the eluate emerges from the tube at about $60cms^{-1}$. This causes turbulence in the cell which must be dampened or the different fractions separated from the column will be mixed together. By experimenting using dyes to show the flow patterns it was found that the best shape for the tube was conical at the base.



This restricts the volume over which turbulence can occur. The conical section must only be 1cm in length in order that it does not degrade the nmr resolution. Using this configuration the individual fractions pass smoothly past the detection coils.

The cell described above is acceptable from the chromatographic point of view . However as yet we have not mentioned the requirements of the ^{1}H nmr spectroscopy. This demands that the tube must be cylindrically symmetric to a high degree else resolution will be poor. This is achieved by using commercial nmr tubes for the construction of the cells. The two cells tested in detail were as follows:



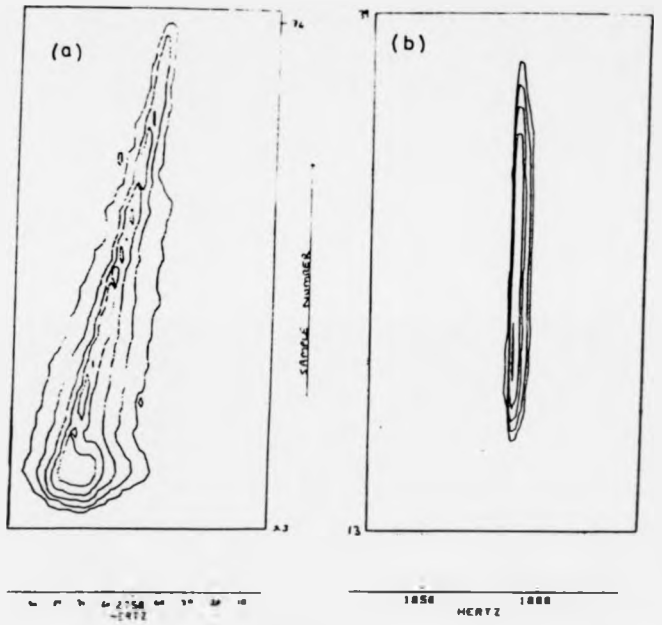
Tube (a) can be "locked" via the anulus of d^6 DMSO but has a smaller sample volume than (b). This does make it easier to achieve good resolution but may reduce sensitivity.

CHARACTERISTICS OF (a) AND (b)

The important characteristic of the cell is the lineshape of a single component in both the nmr and chromatographic dimensions. The narrower these lines are the more sensitive the technique since the lines will be taller. The volume of the region between the coils is also important. This is fixed, the reduction in sensitivity in going from a 5mm tube to a 4mm tube is $4^2/5^2 = 0.8$ i.e. a 20% decrease in intensity.

The lineshapes were recorded by observing the resonance of a sample of benzene in carbon tetrachloride injected into the HPLC system in the normal way. Samples were taken every 0.1 cm^3 in order to get good

definition to the lineshape.



There are 3 principle differences between these resonances:

1) The chromatographic lineshape is much better for (a) due to the reduced turbulence of having a cone shaped tip to the tube.
2) The nmr lineshape is better with a 4mm tube as it has a smaller volume and is easier to "shim".
3) The line for tube (a) is vertical because there is a deuterium lock solvent present. This is a great help for measuring chemical shifts.

The nmr lineshape for tube (a) has a width at half height of about 1Hz however the contour plot shows that it has a very broad base. This could not be eliminated by careful shimming.

It is clear that tube (a) is far superior to (b) even allowing for the

smaller sample volume, therefore it was used in all our latter experiments.

3.14 SENSITIVITY AND LINESHAPE TESTS

In order to test the sensitivity of the system it was set up as for a normal coal run, i.e.

flow rate = $0.3 cm^3 min^{-1}$

solvent : CCl_4

Injection : 100 μL

Column : CN bonded silica (semi prep)

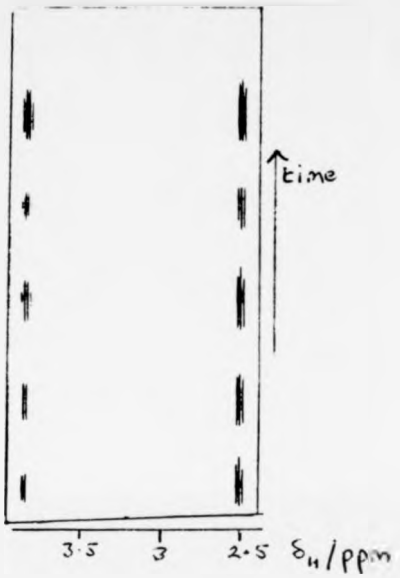
64 samples each of 64 x 8K scans

sample time : 1 minute

A range of solutions of ethyl benzene in carbon tetrachloride of concentrations around the expected detection limit were prepared

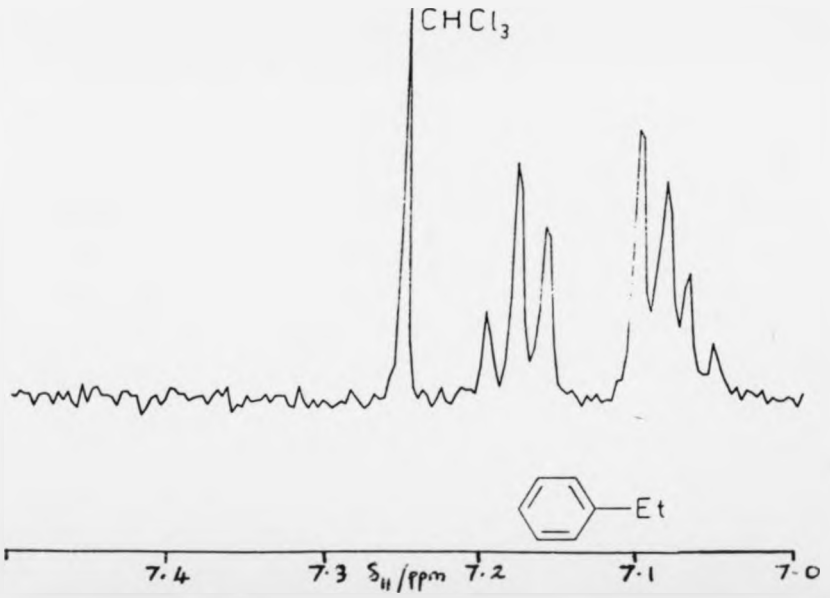
mass of Ethyl benzene in $100 cm^3$ CCl4 (mg)	molarity of solution m. molar	μmoles in 100 μL injection
20	1.8	1.8
70	6.3	6.3
100	9	9
160	14.4	14.4
250	22.5	22.5
500	45	45

and injected at 5 minute intervals. The less concentrated first then in increasing order of concentration. When the data accumulation was over, a Gaussian multiplier was applied to the FID and they were transformed in the normal way.



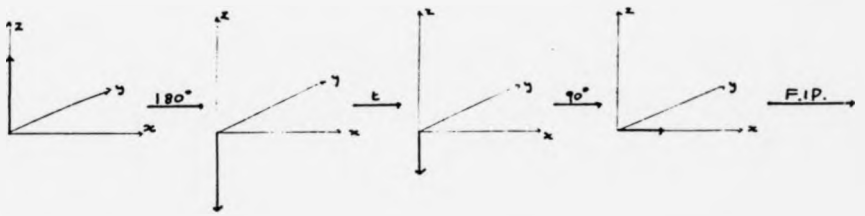
This plot shows 5 of the 6 ethyl resonances of ethyl benzene, showing that the detection limit is in the range 0.2 - 0.7μmoles.

A plot of the aromatic region of the 0.7μmoler sample from this experiment shows clearly the resolution attained. It is clearly at the digitization level or about 1Hz. This is the maximum resolution possible if the accumulation time of a single scan is 1 second.



3.15 AN ESTIMATION OF T_1 FOR AROMATIC HYDROCARBONS

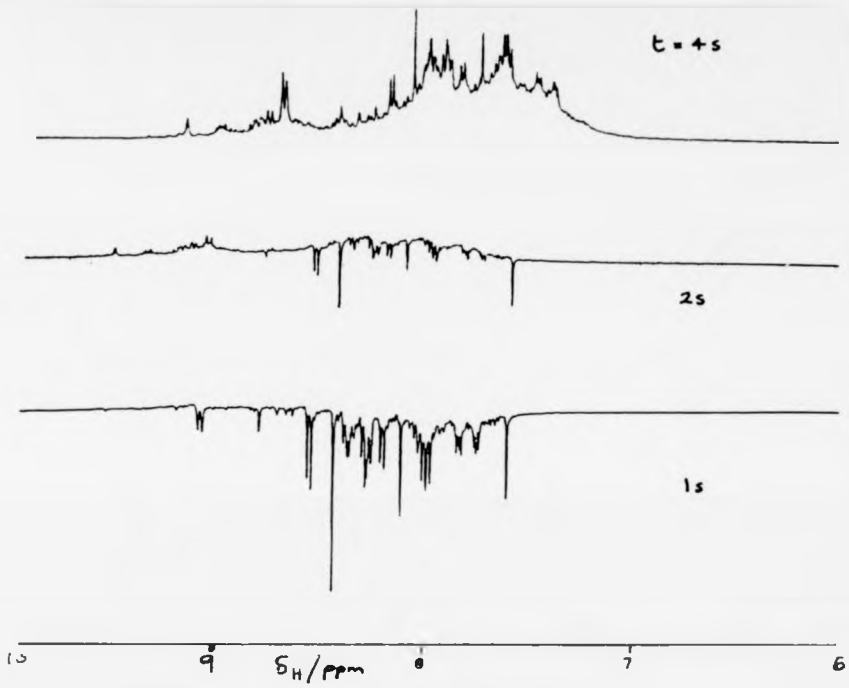
In performing an LC-NMR experiment it is important to know how fast a certain ^1H may become polarized. For essentially complete polarization one must wait 5 x T_1. The longitudinal relaxation rate T_1 of various resonances in a sample of Avenue pitch was measured by the Inversion recovery method.[52] Using the rotating frame vector model for NMR pulses this is as follows.



If t is such that the magnetization has decayed to zero then no signal is observed. This occurs when:

$$t = T_1 \times \ln 2$$

so by recording spectra with different 't' a null may be found and hence T_1 determined. The spectra below show this null for a sample of Avenue pitch dissolved in deuterochloroform.



The null occurs at about t = 2 seconds for the aromatic protons therefore T_1 is

$$\frac{2}{\ln 2} \sim 2\ s$$

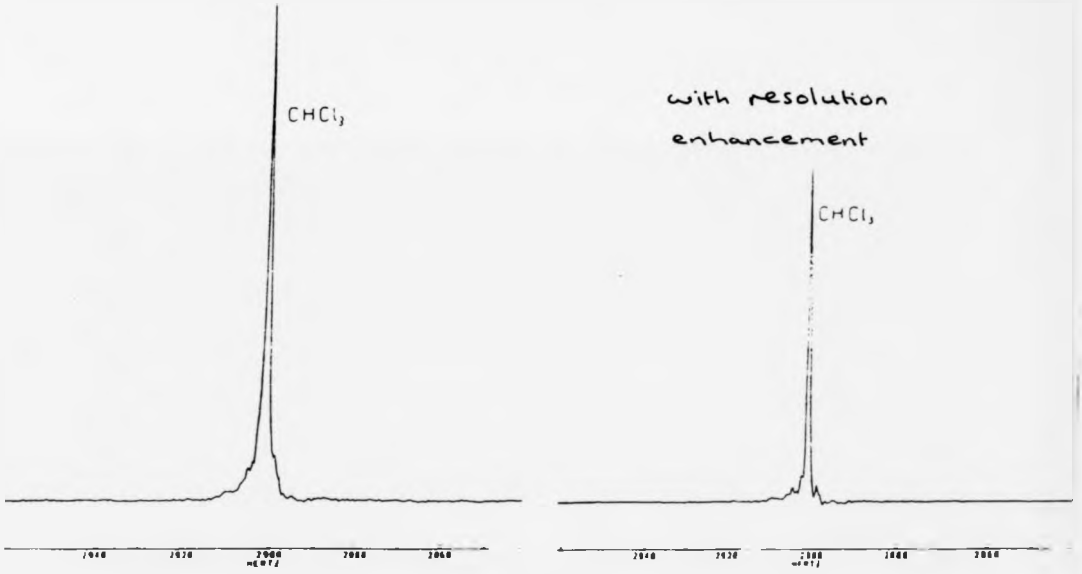
so for complete polarization the sample must be in the magnetic field for about 10 seconds before observation. This corresponds to a volume of $10/60 \times 0.3cm^3 = 0.05cm^3$ or 50 μL. The volume of the cone at the base of the cell is 40 μL therefore as the coils are just above this there is sufficient time for complete polarization to occur.

3.16 SHIMMING

One of the major problems with LC-NMR is achieving a good lineshape for solutions in a stationary and assymetric sample tube. The magnetic field was adjusted using the Golay coils ("shims") as follows.

A 5% solution of chloroform in carbon tetrachloride was pumped into

the cell using the high pressure pump which was then switched off. The shims are then adjusted to maximize the FID obtained when pulsing. This is done using a very short pulse so that saturation does not occur. By this method the following lineshape was achieved.

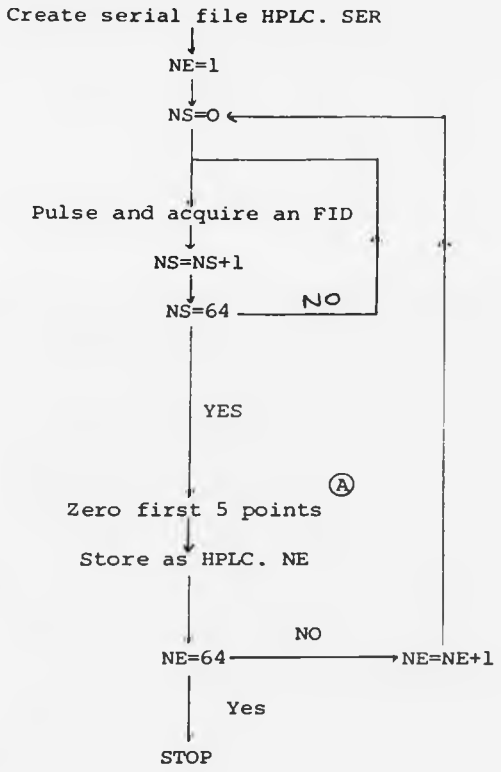


A lineshape this good is unobtainable in practice as flowing fractions from the chromatograph do not have uniform concentration and so the different parts of the sample volume do not contribute equally, this gives a broad base. There is also a broadening due to the motion itself which makes a small contribution to T_2 and hence to the linewidth.

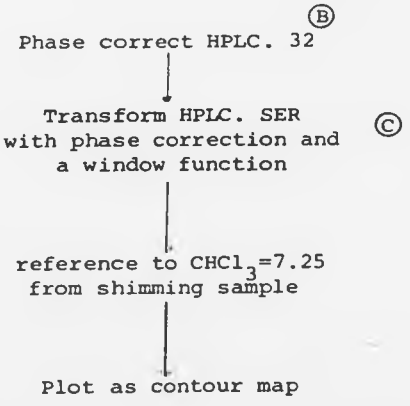
3.17 SPECTRA ACQUISITION AND WORK UP

The spectra were acquired using the program shown below as a flow chart. The spectra were stored in a serial file in order that they could be processed together.

ACQUISITION

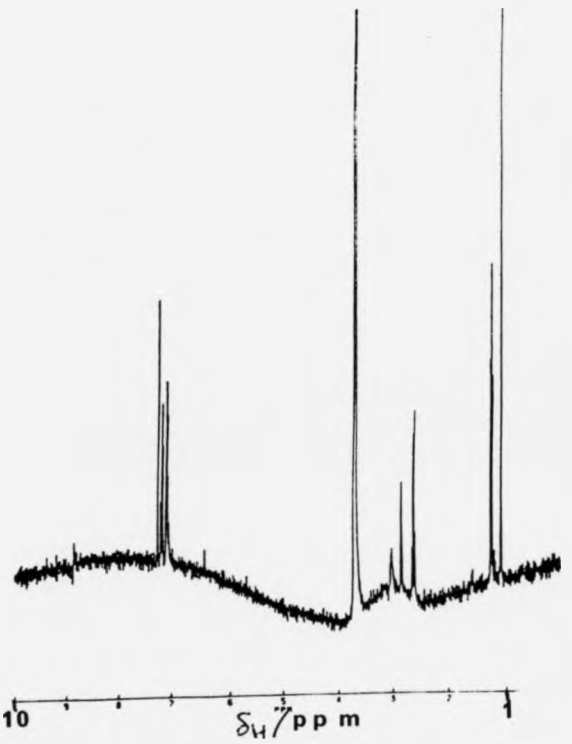


WORK UP



(A) The spectra collected have a tendency to have "rolling" baselines when a large resonance is being observed. For example the spectrum below is of ethyl benzene in CCl_4 but the water present in the lock solvent has caused the baseline to roll.

ETHYL BENZENE IN CCL_4



The problem with this is that small peaks next to a large one are not picked up on a contour plot because the lowest contour is set just above the highest "noise".

This baseline roll is caused by a spike at the beginning of the FID and so zeroing the first few data points reduces it. However this phenomena causes problems in performing LC-NMR experiments as the software does not allow one to use the baseline correction routines on serial files.

(B) All the spectra have the same phase therefore the complete data set may be phase corrected from the corrections from one file determined separately.

(C) Work up: Two window functions were used routinely

(i) An exponential multiplier. This increases signal to noise and reduces resolution by about 1Hz. This is not a serious loss in resolution keeping in mind the digital resolution available.

(ii) A Gaussian multiplier to increase resolution. This was found to be the most generally useful function because it increases the definition on the 2-D plot. The loss in signal to noise is acceptable because the peaks are clearer and easier to interpret.

3.18 METHYLATION OF BERSHAM TAR *

Bersham tar (120mg) was dissolved in THF($10cm^3$), to this was added $1cm^3$ of a 40% aqueous solution of tetra-n-butyl ammonium hydroxide. This solution was stirred for 24 hours after which $1cm^3$ of methyl iodide was added, and the mixture allowed to react for a further hour.

$$R\text{-}OH + (C_4H_9)_4\overset{+}{N}OH^- \ (aq) \longrightarrow R\text{-}O^- + H_2O + (C_4H_9)_4N^+$$

$$R\text{-}O^- + CH_3I \rightarrow R\text{-}OCH_3 + I^-$$

The final reaction mixture was evaporated to dryness to remove CH_3I and THF, it was then redissolved in benzene and filtered, thus removing most of the $(C_4H_9)_4\overset{+}{N}\overset{-}{I}$. The remainder of the iodide salt was removed by successive aqueous extraction. The methylated product was then evaporated to dryness in vacuo, and the extent of methylation checked by ^{1}HNMR.

* This material was produced by the 600°C pyrolysis method described in Section 2.22. The coal was from the NCB coal bank sample from Bersham Colliery. Coal Rank 502.

4. THE NATURE OF SODIUM IN COAL

4.1. INTRODUCTION

Sodium is a relatively minor element in coal with a world average abundance of 0.02%,[53] and a UK range of 0.01 - 0.23%, averaging 0.13%.[54] It is nevertheless of great importance in combustion because of its association with boiler fouling and corrosion. The n.m.r. properties of ^{23}Na are good and so it is possible to observe the sodium in its native state without any prior treatment of the coal.

It is generally accepted that sodium was introduced into coals from saline strata waters after the establishment of coal rank.[55,56] This is consistent with the ease with which sodium may be removed from coal by aqueous leaching.[57-59] Such leaching experiments have shown that sodium and chloride ions are released at different rates and that over 90% of the sodium may be released in this way. The exact mode of occurrence of sodium remains uncertain but is probably not as NaCl crystals as once thought. Saunders[60] proposed that the sodium is present as NaCl(aq) in the coal micropores, probably in the form of ions and water molecules adsorbed on the pore walls, but the possibility of sodium being attached to the organic matter in Australian brown coals was suggested by Durie.[61] Our work has shown by direct observation of the sodium environment that sodium ions are bound both to the organic matter of coal and to water molecules adsorbed in coal pores, this is also the resulting state of sodium if a coal containing no Na^+ is treated with brine.

4.2 ^{23}Na CHEMICAL SHIFTS

In order to interpret the spectra of coal samples, it was necessary first to get some idea of the chemical shifts expected for different environments. Several chemical shifts for sodium salts in the solid state have been measured previously by Tabeta and Saito.[62] We have greatly increased the number of such shifts, which can be found in Appendix 4 . We wish to understand why a particular salt gives a large or small chemical shift. The chemical shift of a nucleus other than a proton is dominated by temperature-independent paramagnetic deshielding.[63] An interaction between the electron orbital angular momentum and the magnetic field changes the Hamiltonion by:

$$\frac{e\hbar}{2mc}\ \bar{H}.\bar{L}.$$

$\bar{H}$ field strength
$\bar{L}$ orbital a.m.

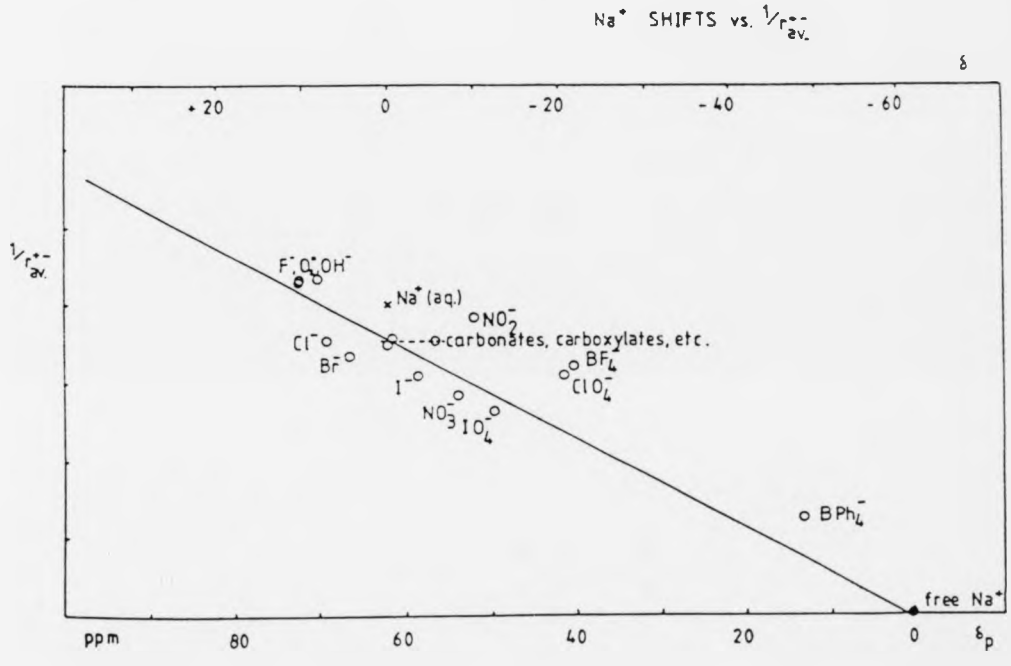
This produced a secondary magnetic field in the same direction as the applied field. It is important to note that there is NO paramagnetic deshielding from 'S' orbitals. As $Na^+(g)$ has L = 0 there is no contribution from paramagnetic deshielding and so it may be used as an absolute chemical shift zero. We may note here that all the chemical shifts observed are deshielded with respect to $Na^+(g)$ = -68.6 ppm, in accordance with this principle.[64]

Although the free Na^+ ion has L = 0, when it is put in a crystal lattice it inevitably becomes distorted. This is equivalent to mixing previously empty 'p' amd 'd' states with the occupied Na^+ orbitals thus giving an induced angular momentum and therefore deshielding.

Table 8

Compound	Interatomic distance (d) A	1/d	1ppm1	Crystal type [65]
NaF	2.31	0.433	+8.0	Cubic: Coordinate
NaCl	2.82	0.355	+7.06	"
NaBr	2.99	0.335	+4.7	"
NaI	3.24	0.309	-3.5	"
$NaNO_2$	Na^+ - N 2.59	0.386	-9.9	
$NaNO_3$	Na^+ - N 3.51	0.285	-8.2	NaCl like: NO_3^- replacing Cl^-
$NaClO_4$	Na^+ - Cl 3.24	0.308	-20.4	6 Coordinate w.r.t. Cl
$Na_2S_2O_3^{(5H_2O)}$	Na^+ - S 2.87	0.348	+0.1	6 Coordinate w.r.t. S
$NaHCO_2$	Na^+ - C 2.84	0.353	-0.2	5 Coordinate w.r.t. C
$NaHCO_3$	Na^+ - C 2.84	0.353	-5.5	
$NaIO_4$	Na^+ - I 3.76	0.266	-12.4	6 Coordinate w.r.t. I
$NaBF_4$	Na^+ - B 3.11	0.322	-21.6	$NaClO_4$ Structure
$NaBPh_4$	Na^+ - B 8	0.125	-48.4	
Na^+ (g)			-68.6	None

In order to try and quantify this effect the crystal type of several sodium salts were collated from the literature. Some of the spectra of sodium salts were not used, either because they contained several sodium resonances or because second order quadrupolar coupling made the chemical shift difficult to determine. The crystallographic data for those salts with simple spectra are given in table 8 . It can be seen from this table that the greater the charge separation in the crystal, the smaller the chemical shift from free Na^+ is found to be. The Na^+ coordination symmetry is not related to the chemical shift in any simple way.



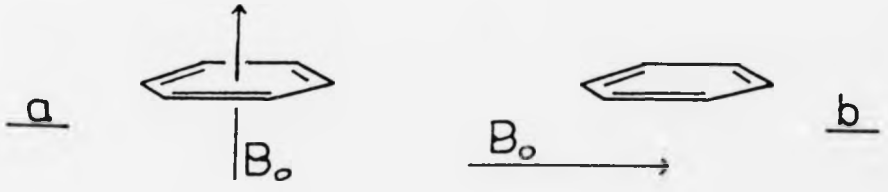
We can see that the chemical shift correlates with the mean reciprocal interionic distance. This is as one would expect, the closer the ions the greater the distribution of Na^+ and so the higher shift observed.

4.3. ^{23}Na MAS nmr

The nuclear spin of ^{23}Na, I = 3/2 means that it has a nuclear quadrupole moment.[66] This is a useful property in solid state nmr work as it ensures that relaxation will be fast and that a high pulse rate may be used. This is not the case for spin ½ nuclei such as ^{13}C, which have very long relaxation times and need cross-polarization techniques in order to be observed easily. Because of the fast relaxation of the sodium nuclei the lines are wide, having a width at half height of $300H_z$ in the case of NaCl. There are two nmr phenomena that illustrate the important differences between solid and liquid state nmr spectra. These are:

(1) CHEMICAL SHIFT ANISOTROPY

The chemical shift of a nucleus depends on the orientation of the molecule containing it with respect to the magnetic field, e.g.



The protons in benzene in orientation (a) experience a secondary magnetic field due to the ring current induced by the static field. There is no ring current in orientation (b). Therefore the

chemical shifts of the protons will depend on the orientation of the molecule. Clearly in a solid one compound may give rise to several chemical shifts on one nuclei due to differences in orientation.

For solution state nmr single lines are observed because the molecular motion averages the various chemical shifts. (see Appendix 3).

The effect of using magic angle spinning is to mimic the molecular motions in liquids and so get a single resonance. This works well provided that the spinning rate is greater than the range of chemical shifts found for different orientations. If this is not the case some narrowing occurs but strong spinning sidebands are observed.[67]

(2) DIPOLAR COUPLING

This is another phenomenon that is averaged out by the molecular motion in liquid samples and is to some extent removed by MAS. However the dipolar couplings in solids can be very large and so this cannot be completely removed by MAS. Dipolar coupling and quadupolar relaxation are the causes of broad Na^+ resonances in pure compounds with only one crystallographic Na^+ site.

4.4. INTERPRETATION OF ^{23}Na MAS SPECTRA

(1) Chemical shift	A large chemical shift implies that the closed shell electrons of sodium are being distorted significantly. The smaller the shift the less distortion is occurring.
(2) Spinning sidebands	The presence of spinning sidebands indicates a very large chemical shift anisotropy and therefore a highly assymetrical environment.
(3) Broad resonances	These are caused by a large number of different species present and or large C.S.A. or fast relaxation.

4.5. ^{23}Na SPECTRA OF RAW AND DRIED COALS

A large range of British and overseas coals were investigated by ^{23}Na MAS nmr. All the coals containing 0.04% sodium gave genuine resonances which were single sharp peaks within the shift range δ = +.3 to -1.7 ppm.

Table 9

Analyses of the Coals

Coal	Origin	Proximate analysis, % ad				Ultimate analysis, % dmmf						Ash analysis, % ad, on coal		
										% db				
		Moisture	Ash	Vol. Matter	Fixed Carbon	C	H	O	N	S	Cl	Na	K	A
Cynheidre	UK	1.6	1.8	4.6	92.0	95.2	2.9	0.9	1.0	0.6	0.03	0.02	0.01	0.
Taff Merthyr	UK	0.8	4.0	12.7	82.5	92.4	4.2	1.6	1.5	0.7	0.05	0.08	0.01	0.
Tilmanstone	UK	0.7	5.4	16.0	77.9	92.4	4.5	2.0	1.5	1.2	0.08	0.04	0.10	0.
Cwm	UK	0.7	5.9	20.9	72.5	90.3	4.4	2.9	1.5	0.8	0.02	0.02	0.01	1.
Cortonwood	UK	1.0	2.2	34.7	62.1	87.2	5.6	3.9	1.7	1.0	0.09	0.02	0.01	0.
Buller	New Zealand	1.3	0.2	35.3	63.2	84.9	5.4	6.6	1.3	0.7	0.09	0.01	<0.01	0.
Cresswell	UK	2.4	2.2	36.2	59.2	84.5	5.5	5.9	1.9	1.5	0.32	0.06	0.01	0.
Allerton Bywater	UK	4.7	5.2	34.6	55.5	83.2	5.4	8.0	1.7	1.7	0.34	0.11	0.10	0.
Linby	UK	9.8	6.2	31.8	52.2	83.0	5.5	8.7	1.9	1.9	0.44	0.16	0.16	0.
Littleton	UK	6.1	4.9	35.7	53.3	82.9	5.2	8.9	1.6	1.1	0.67	0.09	0.07	0.
Lea Hall	UK	8.0	3.1	35.5	53.4	82.6	5.3	9.1	1.6	0.8	0.80	0.16	0.01	0.
Gedling	UK	10.0	2.0	34.5	53.5	81.6	5.2	9.4*	1.7	1.0	0.46	0.11	0.01	0.
Saskatchewan lignite	Canada	22.2	12.8	38.0	27.0	71.5	4.7	21.7*	1.1	1.0	0.03	0.03	-	1.
Texas lignite	USA	13.0	15.6	46.9	24.5	70.3	6.2	21.3*	1.0	2.4	0.02	0.01	-	1.
Australian brown coal	Australia	28.7	0.9	35.5	34.9	66.9	4.9	26.3*	0.7	0.4	0.42	0.28	-	0.

ad - as analysed (air dried) basis
db - dry basis
dmmf - dry, mineral matter free basis
* - by difference

Table 10

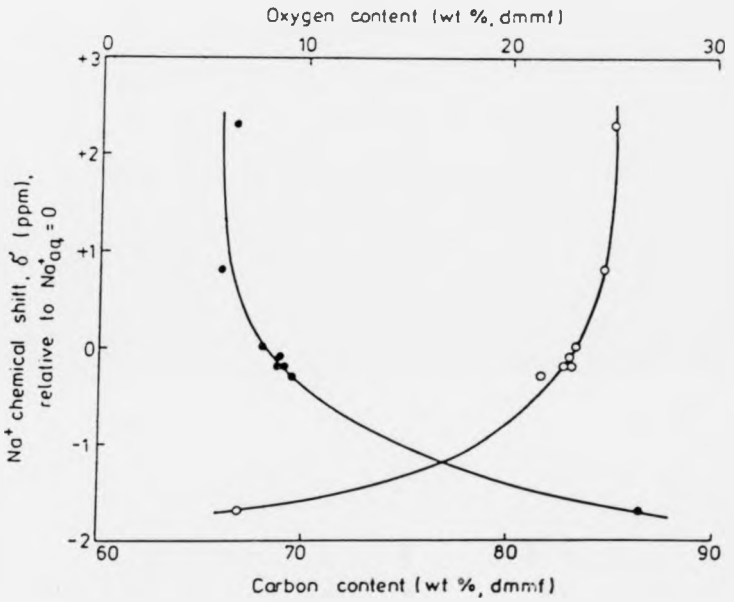
^{23}Na MAS n.m.r. Spectral Data for Raw and Dried Coals

Name	Raw Coal, δ^* (ppm)	Raw Coal, Linewidth (ppm)	Dried Coal, δ^* (ppm)	Dried Coal, Linewidth (ppm)
Buller	+ 2.3	2	-0.9 (+6.5)†	36
Cresswell	+ 0.8	6		
Allerton Bywater	0.0	2		
Linby	- 0.2	2		
Littleton	- 0.1	2		
Lea Hall	- 0.2	2	-5.2 (+7.7)	45
Gedling	- 0.3	2	-11.2 (+7.3)	45
Australian brown	-1.7	4	-15.4	30

* referenced to Na^+_{aq} = 0 at infinite dilution

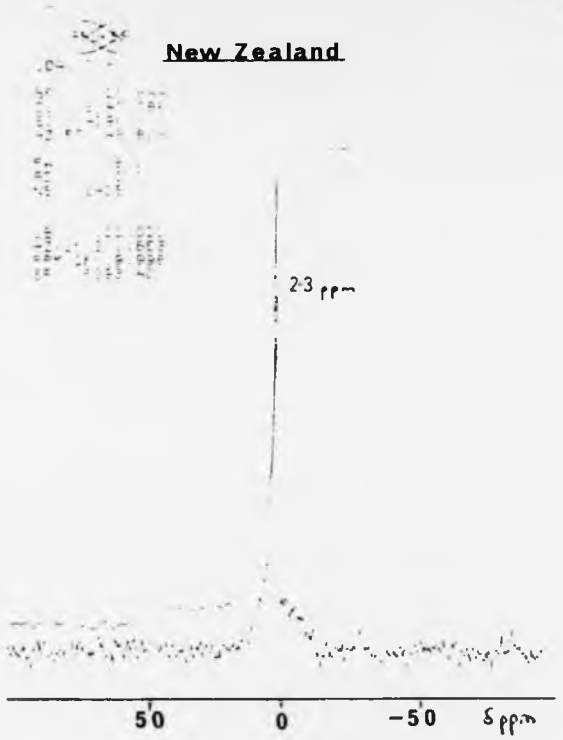
† figures in brackets refer to narrow component

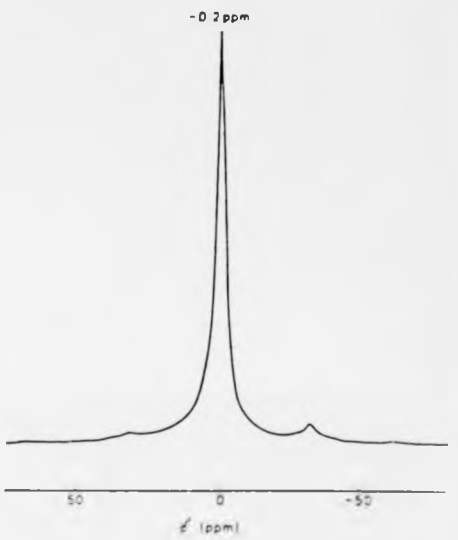
The spectra of most coals show no trace of sodium chloride or of any other crystaline sodium salts. The chemical shifts are instead comparable with that of aqueous Na^+. However there is insufficient moisture in coal to produce sodium ions in true solution. In proof of this, when the spectra were recorded without M.A.S. the resonances broadened considerably, therefore the sodium ions must therefore be motionally restricted. Although the chemical shifts are close to that of aqueous sodium they are not exactly the same, Moreover the chemical shift is dependent on the oxygen content of the coal.

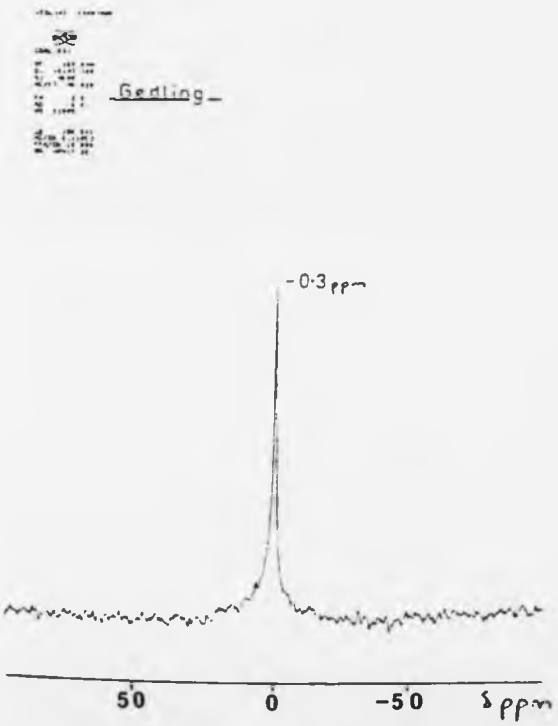


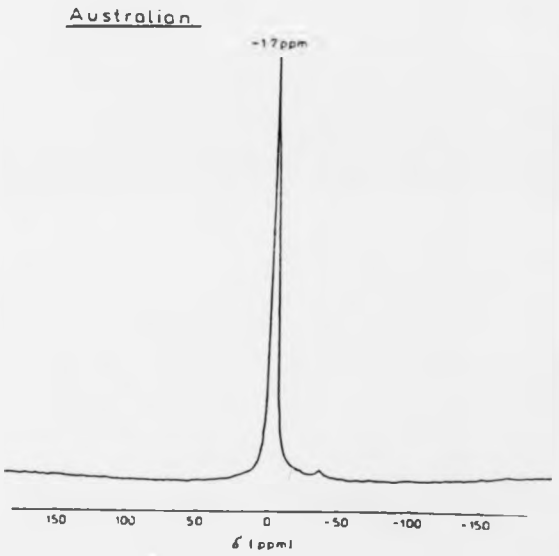
We can picture the sodium ions as been bound to the surface of a coal pore with that pore also containing surficial moisture. This would give resonances at about Oppm but this would also be

^{23}Na SPECTRA OF NATURAL COALS Figure 16









dependent on the nature of the coal itself. This hypothesis was checked by removing the water from 4 coals by heating to 100°C IN VACUO for 12 hours. The spectra of the coals after drying were markedly different. In particular there was a large increase in line width and a change in the chemical shift to low frequency. The shift decrease indicated a reduction in the distortion of the closed shell electrons of Na^+.

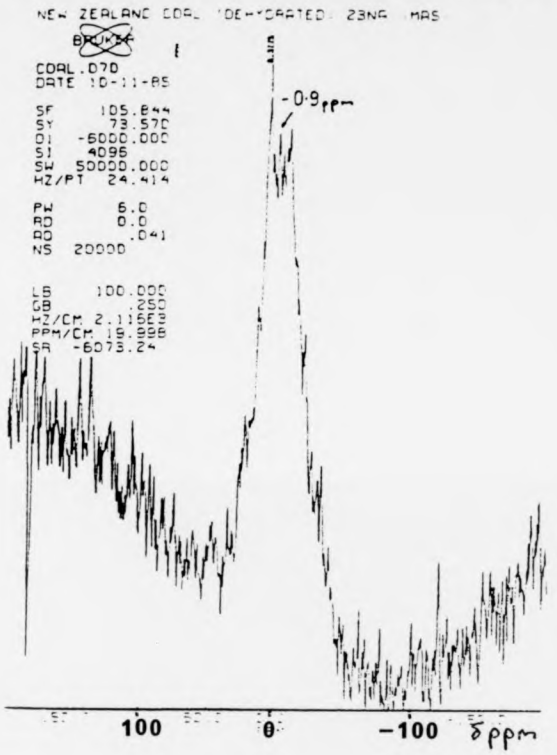
The disppearance of a resonance at 0ppm when water is removed strongly suggests that the water was responsible for the resonance. The chemical shift of the resonance of dehydrated coals is similar to that found for sodium carboxylates and phenoxides and is due to sodium bound to oxygen functionalities on the surface of coal pores. The very low shift found for the Australian coal is probably due to a degree of coordinative unsaturation of the sodium on dehydration.

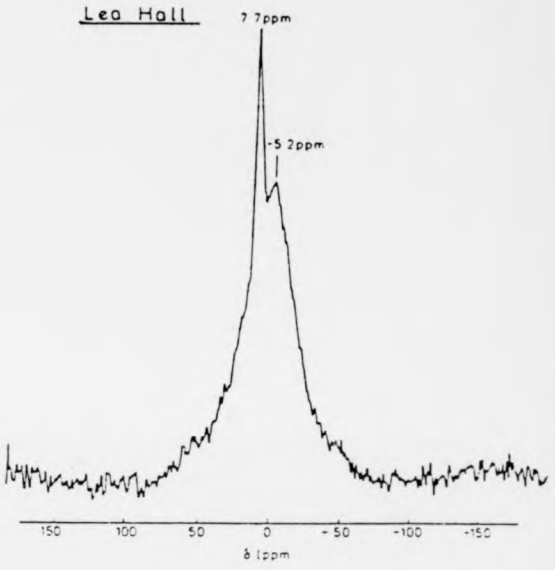
The linewidth of the resonances is indicative of the variety of sites where sodium can be bound to the coal. When moisture is present all the local environments of Na^+ become chemically very similar and so a narrow line is observed.

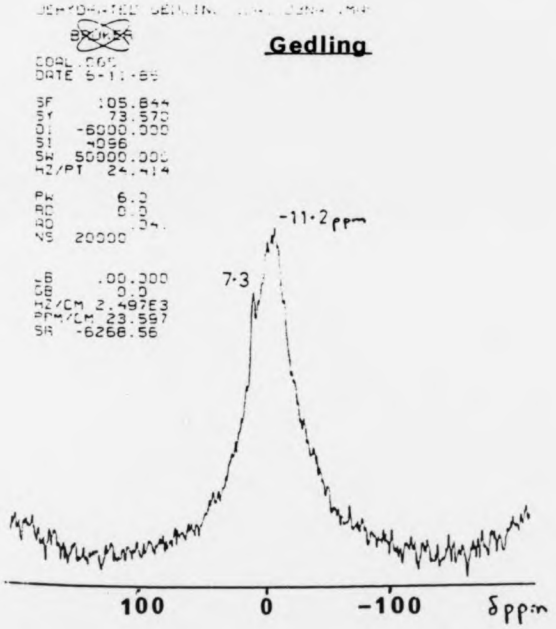
The dehydrated coals of Buller and Lea Hall showed a narrow resonance at around 7 ppm.This is due to the crystallization of NaCl on dehydration. The sodium in this form makes up ~10% of the total sodium content of the coals. These conclusions are consistent with the known case of aqueous leaching of sodium from coal. They do not exclude the possibility of some sodium in a mineral material. This might give a very broad resonance that would not be observed.

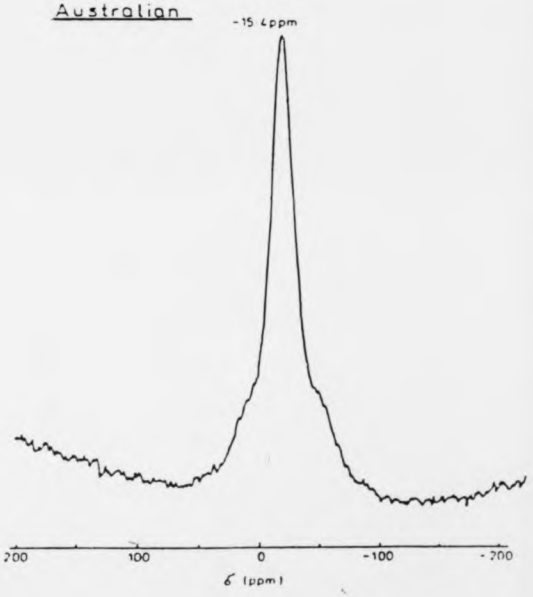
^{23}Na SPECTRA OF DRIED COALS

Figure 17

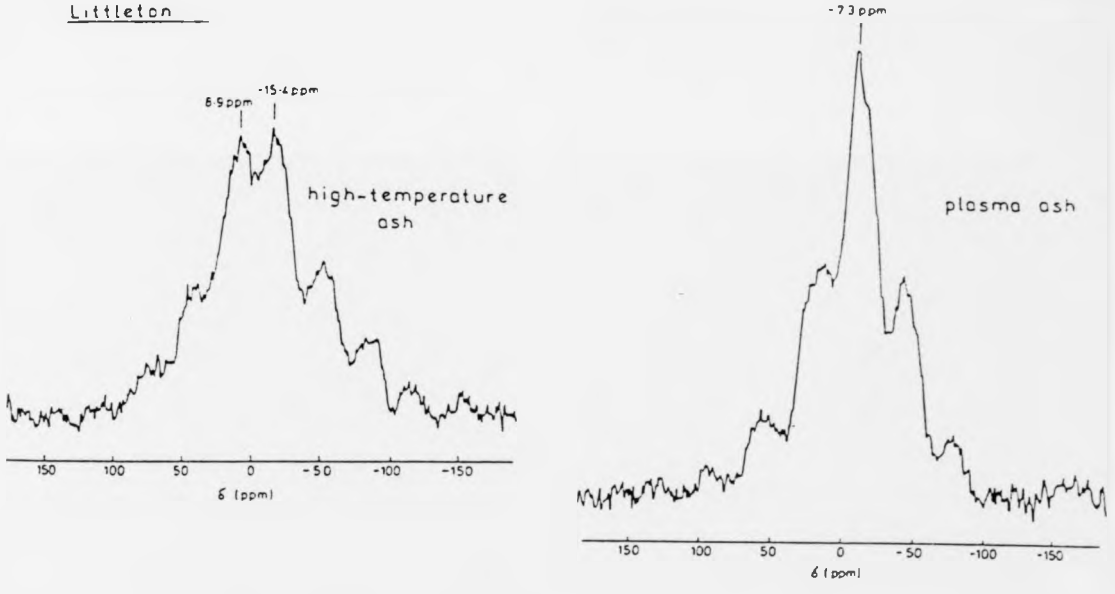








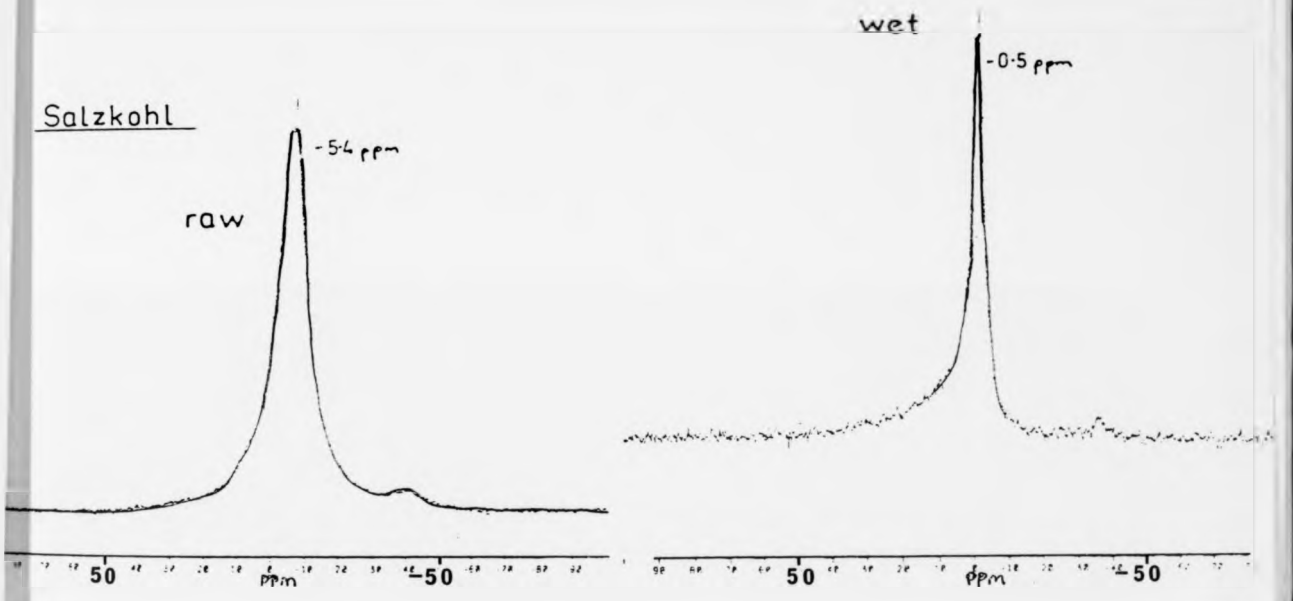
If the sodium is associated with the organic matter in coal as we have asserted, then when the coal is burnt the sodium spectra should be completely changed, and some **intensity** lost.



The low temperature plasma ash of Littleton coal was subjected to ^{23}Na n.m.r. This showed that the environment changes and that the sodium is not held in mineral matter. It also showed considerable loss of Na^+, judging from the signal strength in comparison with that anticipated on the assumption of only C, H and O being lost. The plasma-ashing process leaves most minerals completely unchanged. The ^{23}Na spectrum of a high temperature ash is different again. This shows that on heating to $1000^{o}C$ the remaining sodium reacts with the mineral matter present.

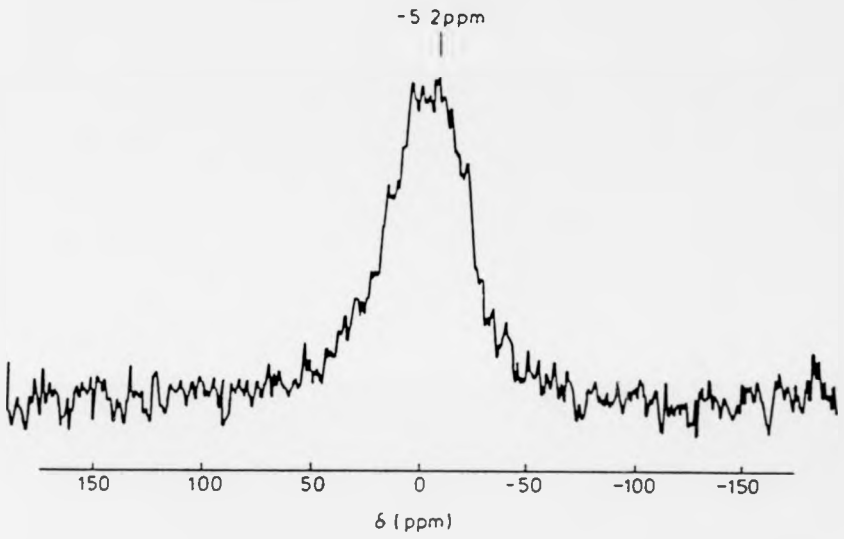
Given that we understand the nature of sodium in coal we were interested in what happened if a coal had a very high salt content

such as in an East German salt coal (NaCl ~5%).



In this case the salt content is so high that the coal appears dehydrated in its raw state and only by wetting could a more normal coal spectrum be observed. As with all the other coals observed the dehydration or wetting experiments were completely reversible.

The last remaining question is how did the sodium get into the coal in the first place? It has long been assumed that the sodium entered coal from saline strata waters after the establishment of coal rank. We checked this hypothesis by treating a powdered low sodium coal (0.04%) with brine ($30 gl^{-1}$ comparable to seawater) then observing the ^{23}Na spectrum of the dehydrated coal.



This spectrum is very similar to those of untreated dehydrated coal and is consistent with the view that brine entered the coal in the later stages of coalification. In particular the spectrum shows little sign of NaCl.

4.6. CONCLUSIONS

1) Sodium ions are surface bound to coal and hydrated in the natural state.

2) Dehydration does not in general cause the sodium to crystallise as sodium chloride; rather it remains bound to the coal, and some coordinative unsaturation may occur.

3) Ashing destroys the Na^+ environment, which shows that this is not mineral.

4) The sodium addition experiments suggest that coal acts as an ion-exchange medium, so that even after treatment with NaCl(aq) and subsequent drying the resulting Na^+ is found predominantly in forms other than crystalline NaCl.

4.7. RECORDING ^{23}Na M.A.S. NMR SPECTRA

^{23}Na n.m.r. spectra were run at 105.8 MHz with magic angle rotation at between 2 and 3 kHz using a Bruker WH400 spectrometer. The rotation angle was adjusted by observing the ^{79}Br resonance of KBr and maximizing the F.I.D. The raw and dried coal samples typically required 20,000 transients using a sweep width of 50,000Hz. Some problems were encountered with contamination of the probe-head, giving rise to a broad ^{23}Na signal when no sample was present. As this resonance could not be completely eliminated even after careful cleaning, the low sodium coals were recorded by subtracting a background spectrum from the sample spectra. Using this procedure no genuine sodium signals were found for coals containing $< 0.04\%$Na.

4.8. CHEMICAL SHIFTS

The shift standard is aqueous sodium ion at infinite dilution. By successive dilutions this was found to be -0.1 ppm from 2M NaCl(aq), which is a good practical standard.

4.9. SAMPLE PREPARATION

i) Coal Samples

The coal samples were examined by ^{23}Na M.A.S. N.M.R. after crushing and screening to 212μm. These samples were not stored under nitrogen and so had a significant moisture content (see table 9). This was removed by heating to 100^{o}C under vacuum overnight and the change in ^{23}Na spectra between raw and dried coals observed. The dried coals were loaded into the rotors in a dry-box as they were very hygroscopic.

In order to test the hypothesis that the sodium content of coals comes originally from brine, two coals showing no detectable ^{23}Na resonance were soaked in brine ($30gl^{-1}$, comparable with seawater), washed rapidly during filtration and exhaustively dried. The coals were then studied by ^{23}Na NMR.

ii) Coal ash

The ^{23}Na spectra of the high temperature and plasma ash of Littleton coal were recorded. The high temperature ash is produced under conditions typically found in coal-fired boilers and is the residue from combustion. The low temperature plasma ash was produced using a Plasmaprep 300 unit at 100W. This device burns the organic matter at $\sim 150^{o}C$ but is thought to leave the mineral matter unchanged.

iii) Standards

The chemical shifts of many sodium salts were recorded using ^{23}Na MAS N.M.R. The samples were from various commercial sources. The spectra required only 100 transients to give good signal to noise.

CHAPTER 5 CONCLUSIONS

The purpose of this work has been to develop N M R. techniques for use in elucidating coal structure, with emphasis on the heteroatoms present in coal

Our investigations of various derivatization methods led us to choose the ^{29}Si N.M.R. signal of trimethyl-siloxyl groups for the investigation of hydroxyl groups in coal products. It was found that the silicon chemical shifts of these groups were directly related to the acidities of the parent compound. This allows one to describe the local environment of the hydroxyl groups in terms of both functional groups and the electron withdrawing effect of the system they are bound to. Using this method we have described the hydroxyl environment in a supercritical solvent extract of Daw Mill coal, and in a rank series of coal tars. These results have been interpreted in terms of peripheral groups that are released from the coal matrix during pyrolysis, and discussed in relation to a model coal structure, and the process of coalification. The principal conclusions are that;

1) Phenols are essentially the only hydroxyl types

present in mid-high rank coals although low rank coals and coal precursors have a wide variety of hydroxyl types.

2) The changes in composition of the tars with rank have been described in terms of changes to the peripheral groups with age These changes are of two types. The first is the change in the nature of the groups themselves, described above. The second is that the rate at which such groups become consolidated into the coal matrix during coalification is dependant on their structure. We have seen that the highly alkylated phenols become incorporated into the involatile matrix more slowly than the less alkylated phenols, probably because steric hinderance about their hydroxyl groups inhibits cross-linking.

3) Derivatisation of hydroxyl containing samples with H.M.D.S and observation of the silicon resonance is the method of choice for identifying acids, phenols, and alcohols in complex solutions by N.M.R. spectroscopy.

The work on L.C.-N.M.R. was pursued as an attempt to try and simplify the proton spectra of coal products by separating their components immediately prior to observation. This technique is not new, but has not been applied before to coal tar fractions.

It has always been assumed that one must build special N.M.R. probes in order to acheive sufficient sensitivity. This is not so, as we have seen that without such probes a sensitivity of 0.5μmolar and an N.M.R. resolution of 1 Hz can be acheived. This is sufficiently sensitive to identify many components in complex coal products. In particular it allows the separation and identification of some isomers that could not be acheived by gc-ms. Analysis of such complex samples by L.C.-N.M.R. has not been done by previous workers.

We have used ^{23}Na M.A.S.-N.M.R. to determine the environment of sodium in coal. This was done by the analysis of the line-shapes, and chemical shifts of raw and dried coals, and a comparison with those of standard compounds Our conclusions were that sodium is coordinated both to oxygen functionalities on the surface of a coal pore, and with moisture contained within that pore. When dried some coordinative unsaturation of the sodium ions was observed. Our attempts to add sodium ions to a previously sodium free coal by soaking in brine were consistent with the view that the sodium in coal came from exposure to sea water. No sodium was observed in a mineral form or as sodium chloride crystals, and only traces of salt were observed even in the dried coals

APPENDIX 1

POLARIZATION TRANSFER TECHNIQUES

In this section we will describe how the INEPT experiment used for detecting silicon resonances work. In order that the ideas are clear we will consider an isolated Si-H system and use the rotating frame vector model to describe the magnetizations involved.

I.N.E.P.T.[31]

^{1}H D1 - 90° - D2 - 180° - D2 - 90° - D3 - 180° - D3 - BB

^{29}Si 180° 90° 180° F.I.D.

D1: A relaxation delay to allow 5T for proton recovery.

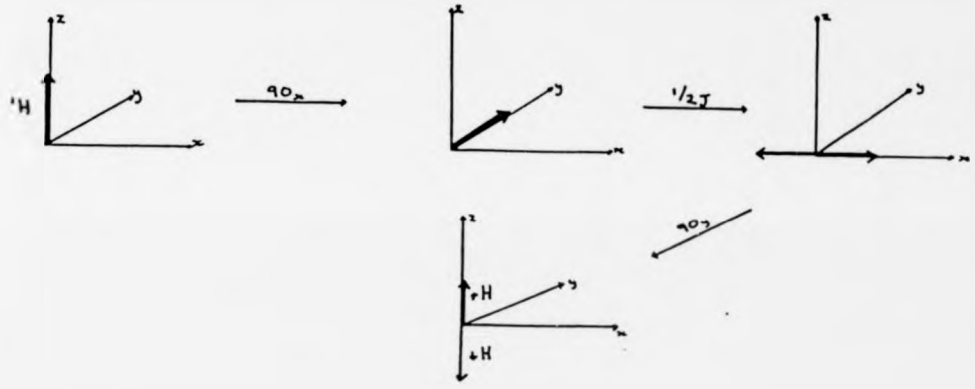
B.B. : indicates that the spectra are acquired with Broad Band ^{1}H decoupling.

In considering this pulse sequence one may ignore all the 180° pulses; these are used to refocus chemical shifts during the experiment so that all resonances respond equally. The important sequence is:

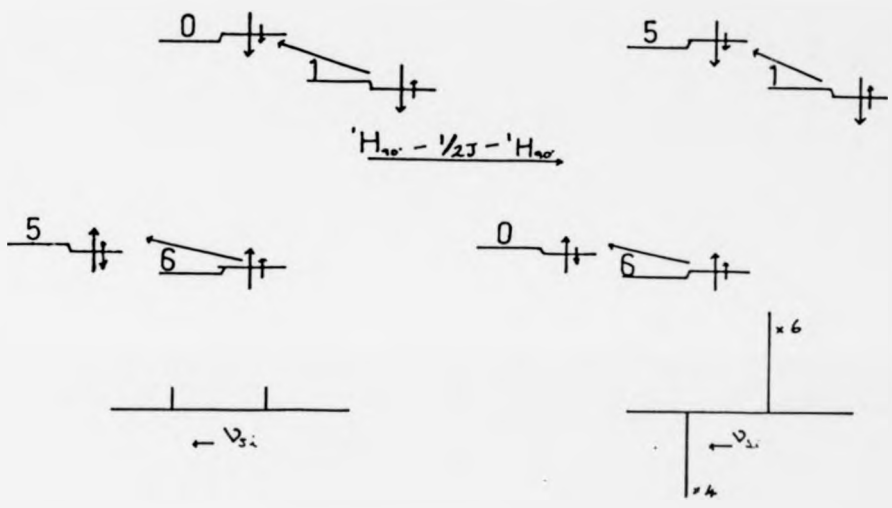
^{1}H 90° - 1/2J - 90° - 1/2J - BB

^{29}Si 90° F.I.D.

Effect of ^{1}H pulses

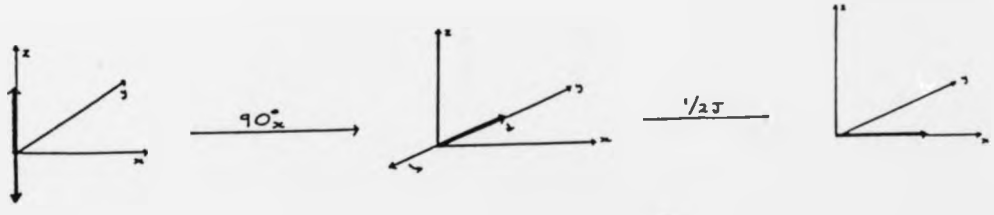


As can be seen from the diagram the effect of these pulses is to cause a population inversion for those spin states with silicon spin down. This has two major effects on the silicon transitions (see below). Firstly the resonances have become far more intense, and secondly the high frequency line has been inverted.



(The figures are the relative excess populations of each spin state).

From the silicon spectrum it is clear that the silicon spins are as shown below. The 90° pulse and subsequent delay cause the two components of the silicon resonance to refocus before observation. The final increase in sensitivity over a simple decoupled spectrum is a factor of 5.



Progress of silicon magnetization during the INEPT sequence

APPENDIX 2 (i)

ULTIMATE ANALYSIS OF SUPERCRITICAL EXTRACT FRACTIONS

Description	C %	H %	N %		O %		S%	MW (av)	% of whole coal
			Total	Basic	Total	OH			
CR18 unfractionated	83.3	6.4	1.05		7.1		0.96		35
Pentane solubles	86.3	8.0	0.30	0.18	5.3	3.1	0.95	220	21.6
Pentane Sol. acids					13.1	9.3			
Pentane Sol. bases			15.5						
Asphaltenes	81.4	6.1	1.14	0.49	7.7	6.2	1.13	520	21.6
Asphaltene acids						10.2			
Asphaltene bases			5.1	2.61					
Benzene Insolubles	81.0	5.2	1.59	0.70	8.0	8.1	1.20	1270	21.6

CR18 was produced by CRE by extraction of Daw Mill (CRC 902) coal at 450°C and 200 tar with toluene. A coal to solvent ratio of 1:10 produced an extract representing 37.2% (d.a.f.) of the original coal.

Analysis of Daw Mill

Proximate	Moisture % (a.d.)	6.6
	Ash % (d.b.)	13.7
	Volatiles% (d.a.f.)	39.5
Ultimates	Carbon % (d.a.f.)	79.8
	Hydrogen % (d.a.f.)	4.8
	Oxygen % (d.a.f.)	11.6
	Nitrogen% (d.a.f.)	1.4
	Sulphur % d.b.)	1.5
	Chlorine % (a.d.)	0.21

APPENDIX 2(ii)

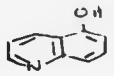
VOLATILE OXYGEN FUNCTIONALITIES AS A % OF THE TAR

	acids	higher phenols	napthols	phenols	alcohols
Tilmanstone	trace	14.8	21	62.2	
Oakdale	2	6	17	75	
Cortonwood		8	26	66	
Linby	1.5	5	26	63.5	trace
Illinois No. 6	3	8	32	57	
Bagworth	2	5	37.5	55.5	trace
Turkish	5	2	11	78	3
Australian	9	10	39	39	3
Peat	27	10	20	39	3
Wood	14	29	23	15	19

APPENDIX 2(iii)

ACIDS	Chemical Shift of Trimethylsilyl derivative	pKa (H_2O)[68]
oxalic acid	29.92	1.27
tartaric acid	28.40, 25.76	3.22, 4.82
chloroacetic acid	27.62	2.86
salicylic acid	26.95	2.75
formic acid	26.00	3.74
malic acid	25.77, 24.39	
2-napthoic acid	25.60*	4.16
1-napthoic acid	25.10*	
lactic acid	24.97	3.86
benzoic acid	24.83	4.20
	24.20*	
p-methoxybenzoic	24.10	4.09
n-hexanoic acid	22.99	4.88
anthranilic acid	23.71	
acetic acid	23.26	4.76

*From a paper by Derepp ref. 30

PHENOLS	Chemical Shift	pKa
o-nitrophenol	24.80	7.21
	23.20*	
p-nitrophenol	22.81	7.16
salicaldehyde	22.66	6.79
m-nitrophenol	22.49	8.38
	22.10*	
1-napthol	20.57	9.30
2-napthol	20.2 ppm	9.57
catechol	20.00*	9.48
phenol	19.43	9.99
m-cresol	19.22	10.09
p-cresol	19.19	10.26
p-amino phenol	18.99	
o-cresol	18.90	10.28
3-t-butyl phenol	18.90	10.18
3, 4 xylenol	18.87	10.32
4-t-butyl phenol	18.77	10.25
2, 5 xylenol	18.69	10.22
2, 6 xylenol	18.49	10.59
2-ethyl phenol	18.41	10.20
2-isopropyl phenol	18.23	
2-n-propyl phenol	18.22	
2-t-butyl phenol	16.91	
2, 6 di t butyl phenol	-- no reaction	

ALCOHOLS	Chemical Shift
methanol	20.07
9-hydroxyfluorene	19.53
n-butanol	19.34
1-acenapthenol	18.09
2-phenyl ethanol	17.92
ethanol	17.13
benzyl alcohol	16.99
n-dodecyl alcohol	16.99
2-methyl propanol	16.96
isopropanol	14.77
butan-2-ol	14.85
t-butyl alcohol	7.56

RESONANCES DUE TO THE DERIVATIZING PROCEDURE

$Si(CH_3)_4$	0.00	- shift reference
$Si(CH_3)_3OSi(CH_3)_3$	2.50	
$[Si(CH_3)_3]_2NH$	7.37	
$Si(CH_3)_3Cl$	31.23	

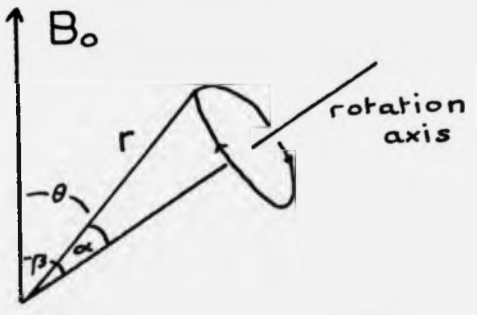
APPENDIX 3

MAGIC ANGLE SPINNING MAS[69]

As mentioned in the text MAS is necessary in solid state Nmr to remove the effects of dipolar couplings and chemical shift anisotropy. Both the Hamiltonian for dipolar coupling and the expression for the isotropic shielding constant σ depend on the geometrical factor $(3\cos^2\theta - 1)$. Where θ is either the angle formed between the 2 spins and Bo, or Bo and a principle axis of σ.

In liquids the molecules are in constant motion and so all values of θ occur. The average of $3\cos^2\theta - 1$ over all θ is zero and so neither of the two phenomena are observed.

M.A.S. causes this geometrical term to become zero by spinning the sample at several kHz about 54.7° to Bo.



The internuclear vectors make an angle with Bo takes all values in a powder sample. It can be shown that the average value of $3\cos^2\theta - 1$ is:

$$3\cos^2\theta - 1 = \tfrac{1}{2}(3\cos^2\beta - 1) \cdot (3\cos^2\alpha - 1)$$

This expression shows that the experimentally set angle β acts as a scaling factor. If is 54.7° the term $3\cos^2\beta - 1$ becomes zero and so the dipolar and chemical shift anistropy effects are removed.

APPENDIX 4

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Compound	Chemical Shift	Reference
$Na^-(g)$	-60.5	
$Na^+(g)$	-68.6	
Na(g)	-63.4	64
NaF	+ 8.0	
NaCl	+ 7.06	
NaBr	+ 4.7	
NaI	- 3.5	
$NaBPh_4$	-48.5	
$NaNO_2$	- 9.9	
$NaNO_3$	- 8.2	
$NaHCO_3$	- 5.6	Warwick
Na_2SO_4	- 1.9	
$Na_2S_2O_3$	+ 0.1	
Na_3PO_4	+ 7.1	
Na_2S	+ 7.1	
NaOH	+10.1	
Na_2O_2	+10.1	
$Na_2SnCl_6 . 5H_2O$	- 6.3	
Na_2PtCl_6	- 6.2	
$NaClO_4$	-20.3	
Na citrate	-13.0	
Na glutomate	- 9.0	
$NaClO_4 . H_2O$	- 7.0	
NaN_3	- 3.5	
$NaH_2PO_4 . 2H_2O$	- 2.7	62
$Na_2WO_4 . 2H_2O$	- 2.7	
Na tartrate	- 0.6	
$NaHCO_2$	- 0.2	
$Na(CH_3CO_2)$	- 0.2	
$Na_4P_2O_2 . 10H_2O$	+ 1.5	
$NaIO_4$	-12.5	

These shifts done at Warwick are referenced to NaCl(aq) at infinite dilution. Otherwise they are referenced to 1 molar NaCl(aq)

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TITLE N.M.R. OF HETEROATOMIC STRUCTURES OF COAL AND COAL PRODUCTS

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